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# LABORATORY MANUAL OF ORGANIC CHEMISTRY

BY

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## PREFACE TO THE FIRST EDITION

The important place which organic chemistry occupies today in the curricula in our Universities has made it necessary to devise a comprehensive course of systematic practical instruction in the subject. Unfortunately, although there is no dearth of manuals written on practical organic chemistry, most of the books are found to emphasise *either* the preparative *or* the analytic aspects of the subject. The need for the student who is just commencing a study of the subject, of a book in which these two elements are judiciously combined has been keenly felt for some time and the present work, the result of experience of teaching the subject for several years, is an attempt in the direction of removing this want. Part I of the book is intended to fulfil the requirements of the elementary student while Part II should be suitable for the advanced students.

In the chapter on the fundamental manipulations, each operation is illustrated with a definite experiment to be performed by the student while a few carefully chosen examples of experiments on the semi-micro scale have been introduced at appropriate places, with the object of training the student in the habit of working with small quantities of materials. The typical reactions for the commoner classes of organic compounds have been given in detail; a familiarity with these is to be considered of great importance as forming the foundation on which the student's skill in organic analysis has to be built up.

The systematic scheme for the identification of the commoner types of organic compounds has been drawn up from experience gained during many years in teaching students who have found little difficulty in classifying and identifying even complex organic compounds with its aid.

The subject of the preparation of derivatives is recognised as an all important one in qualitative organic analysis and it has, therefore, been considered advisable to devote a separate chapter to it. The hints on the choice of derivatives and the details of experimental procedure given wherever practicable, will, it is hoped, be helpful.

The tendency of students to submit scrappy records of organic analysis is a common enough experience and is to be attributed mainly to the students' idea that the spotting of the substance being

his main if not the only problem, the methods of experimentation and observations leading to the typification and final identification of a substance might usually be given a secondary place. This attitude should be discouraged from the beginning and a few model analyses have therefore been given with a view to help the student in picking up the procedure of recording observations systematically and intelligently and drawing conclusions logically.

The preparations of simple organic compounds given in the last chapter have been chosen so as to illustrate the main reactions in organic chemistry, e.g., esterification, hydrolysis, oxidation and reduction etc. In no case have theoretical explanations of the reactions been given. This should clearly be learnt by the student from his theoretical text-books, the space saved thereby being more usefully employed in giving practical hints. The yields given for each preparation are those actually obtained by the students working in this laboratory.

The second part contains chapters on the quantitative estimations of typical groups, the qualitative separations of mixtures of which a few examples are described in detail, organic preparations of an advanced character involving a number of steps and illustrative of special reactions, and finally the quantitative determination of the elements with a full description of the semi-micro methods of Bobransky and Sucharda, slightly modified, for estimating C, H and N, which are being used with success and are very popular with the students in this laboratory.

The appendices given at the end of each part contain much valuable information and are intended for frequent reference.

In writing this book standard works like Mulliken's "Identification of pure Organic Compounds", Thorpe and Whiteley's "Manual of Organic Chemical Analysis", Gattermann's "Laboratory Methods of Organic Chemistry", Emich's "Micro-chemical Laboratory Manual", etc., have been freely consulted. Our grateful acknowledgments are made to the authors of these works.

Our thanks are also due to some of our colleagues for help in the work of reading proofs and to those of our students who prepared at our request several of the compounds described in the second part.

*Presidency College, Madras.*  
*June, 1937.*

B. B. DEY  
M. V. S. RAMAN

## PREFACE TO THE SECOND EDITION

The reception accorded to the first edition of the book which is now exhausted has encouraged the authors to bring out a second edition of the first part for the present. No changes of a fundamental character have been made and the original plan which has been found to be satisfactory has been retained. The only chapters where a rearrangement and addition of matter have been considered necessary in the light of experience gained from the use of the book and of suggestions received from colleagues in other colleges, are those on "Reactions of common organic compounds" (Chapters III & IV), "Preparations of derivatives" (Chapter VI) and "Organic preparations" (Chapter VIII). The last chapter has been slightly enlarged by including about a dozen new preparations of a representative character so as to offer a wider choice, without making the book unnecessarily voluminous.

*Presidency College, Madras,*  
*October, 1941.*

B. B. DEY  
M. V. S. RAMAN

## PREFACE TO THE THIRD EDITION

The second edition of this book brought out in 1941 has been out of print for many years now. The book had been found to be of great value by most laboratories in India imparting instruction in practical organic chemistry. The late Prof. M. V. Sitaraman had been carrying out a revision for the purpose of bringing out a third edition, a work unfortunately cut short by his untimely death. The completion of this task was undertaken at the request of Prof. B. B. Dey. Material in the original book has been largely retained, since it is the outcome of the long experience of the authors in imparting instruction in practical organic chemistry. Directions for the preparation of several new types of derivatives useful in the characterisation of various functional groups have been included. Forty six new preparations have been added illustrating types of organic reactions not dealt with in the original book. The section on quantitative analysis has been expanded by the addition of several new exercises. Methods for the preparation of various pure solvents and reagents have also been included. No attempt has been made to make the book encyclopaedic, but it is earnestly hoped that it will prove useful to students both in the B.Sc. and M.Sc. classes in carrying out work in practical organic chemistry. Even the research worker should find in this book many items of interest.

This revised edition is not officially sponsored and this book is not an official publication.

*Presidency College, Madras,  
26th June 1957.*

*T. R. GOVINDACHARI,  
Chief Professor of Chemistry.*

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## INTRODUCTORY

### GENERAL PRECAUTIONS TO BE OBSERVED IN PRACTICAL ORGANIC WORK

(1) Extreme caution is necessary in the use of ether, carbon disulphide, light petroleum, alcohol, acetone, benzene etc., as the vapours of these are highly inflammable. Care should be taken to have no flame burning in the neighbourhood. These should always be distilled on a water-bath, preferably electrically heated, using long condensers and, if necessary, ice water for cooling the receiver. If the liquid in a beaker or a flask catches fire, as is often the case during crystallisation, the flame should be extinguished by covering the beaker or flask completely with a watch or a clock glass.

(2) All experiments in which fumes or noxious vapours are evolved should be conducted in a fume cupboard. Care should be taken not to inhale vapours of fuming acids, cyanogen, hydrocyanic acid, carbon monoxide, dimethyl sulphate etc.

(3) Bits of sodium residues should not be dropped into the sink, but should be dissolved in alcohol and when all action has ceased, the solution should be poured into the sink.

(4) It is advisable to protect the eyes with goggles or even plain glasses in all vacuum and pressure work and during operations with explosive substances.

(5) **Accidents : Fire.** The laboratory should be provided with a fire extinguisher and also a few buckets of sand. A heavy woollen blanket is very useful in case the clothing catches fire and should be kept within easy reach.

*Remedies for the following commoner accidents in the laboratory :*

(a) For burns : By heat. The part should be covered with carron oil or painted with an aqueous solution of picric acid.

Carron oil is made by shaking equal parts of raw linseed oil and lime water. Cocoanut oil may also be used instead of linseed oil.

For large burns always apply acriflavine emulsion, and cover the affected part, either the hand or the arm with sterilised cotton, soaked also in the emulsion. A saturated aqueous solution of picric acid can be employed as well.



(b) For acid burns : On the skin. The affected part is washed with plenty of water and then with dilute sodium bicarbonate solution. Finally carron oil should be applied.

In the eye. A filtered solution of boric acid should be taken in the eye-glass and applied to the eyes.

(c) For alkalis : On the skin. The affected part should be washed with plenty of water and then with weak acetic acid (1%).

In the eye. Saturated boric acid solution and a little castor oil should be applied as before.

(d) For bromine : On the skin. Alcohol and carron oil are to be applied successively.

All these remedies should be kept handy in an easily accessible place.

(6) For quick work the student should have a definite plan and a clear idea of what is going to be attempted during the day, omitting nothing that might be necessary.

(7) In the case of a preparation, the theory as well as the practice of the entire method should be thoroughly studied previously.

(8) All apparatus for the next day's work should be cleaned even on the previous day and left for drying.

(9) Vessels appropriate to the quantities of substances taken should be used.

(10) Apparatus should be fitted up neatly and compactly paying particular attention to the boring and fitting of corks.

(11) Observations should be made with great care and recorded systematically and immediately.

(12) All samples of organic substances prepared in the laboratory should be preserved in labelled specimen tubes, if solid, and in sealed tubes, if liquid. The label should show the yield and the physical constants. The question of yield is to be considered an important point in all preparations, an operation being said to be successful only when a good yield of pure product is obtained. The use of an unnecessarily large number of vessels should be avoided because if a small amount of the reacting mixture (say 2 to 3 per cent.) is left in each vessel, the final yield of the product will be considerably diminished.

## CHAPTER I

### SIMPLE OPERATIONS IN PRACTICAL ORGANIC CHEMISTRY

Before commencing a course in practical organic chemistry, the student should acquire skill in the practice of some of the common operations which are peculiar to such work. These fundamental processes can be classified into four types, viz., (1) Crystallisation and (2) Sublimation, applicable to solids ; (3) Distillation, applicable chiefly to liquids ; (4) Extraction by a suitable solvent, which is applicable to solids as well as liquids. An organic compound, when prepared in the laboratory, is seldom obtained pure. It is often admixed with traces of other compounds due to side reactions. Before commencing the analysis of an organic compound, the student should be certain of its purity--*i.e.*, he must know that he is dealing with a single compound. The purification process, therefore, forms an important part of laboratory work in organic chemistry.

**1. Crystallisation.** Impurities associated with a solid are almost always removed by this process which should be applied with great care, so as to obtain the maximum yield of the purified compound.

The choice of a suitable solvent is often a troublesome task, but information is generally available as to the proper solvent to be used in the cases of several known compounds. In other cases, the solvent has to be determined by trial. The solvent chosen should (a) not react with the solute chemically, (b) hold in solution a fairly large amount of the solute at a high temperature, (c) keep back as much of the impurities as possible and deposit only the pure compound from the mother liquor on cooling. The solvent should not be highly volatile nor should it, as a rule, boil at a temperature higher than 130°. Easily inflammable solvents should, as far as possible, be avoided, or used with the greatest possible care.

**Method of finding the solvent by trial.** About 0.1 gm. of the finely powdered substance is placed in each of a number of clean dry test-tubes ( $4'' \times \frac{1}{2}''$ ) and treated with a few drops of

the solvent, the volume of the solvent added never exceeding 1 c.c. in each case. The solvent which dissolves the substance completely near the boiling temperature, and deposits on cooling most of the dissolved substance in a crystalline condition, should be chosen. This method is very useful when analysing an unknown organic compound.

The solvents commonly employed for crystallisation are water, alcohol, ether, benzene, petroleum ether, acetone and glacial acetic acid. In special cases chloroform, ethyl acetate, xylene, pyridine, nitrobenzene etc., are also used. Each one of the above solvents can be restricted to one or two types of substances so that one can get an idea of the solvent to be used for a particular substance. Thus the following table gives a general idea of the solvent to be employed for different types of substances :

**Common solvents for crystallization**

Solvent or solvent pair	Types of compounds
Water ...	Carboxylic acids, amides and substituted amides
Methanol ...	Most derivatives ; benzoates, 3, 5-dinitrobenzoates, amides, <i>p</i> -toluidides, nitro and bromo compounds etc.
Methanol-water ...	Sulfonamides, anilides, picrates, semicarbazones, hydrazones, substituted hydrazones etc.
Ethanol ...	Same as methanol and methanol-water mixtures, molecular compounds.
Petroleum ether ...	Phenylurethans, $\alpha$ -naphthylurethans.
Acetone-alcohol ...	Osazones, bromo compounds, nitro compounds
Benzene ...	Picrates, molecular complexes.

Sometimes a mixture of two solvents is found to be more satisfactory than a single solvent. It is necessary that the substance should be more soluble in one solvent than in the other. The most useful mixtures are water-alcohol, chloroform-light petroleum, alcohol-ether and benzene-ligroin.

close by and the steam generator should be kept at a safe distance. If the substance shows a tendency to crystallise too

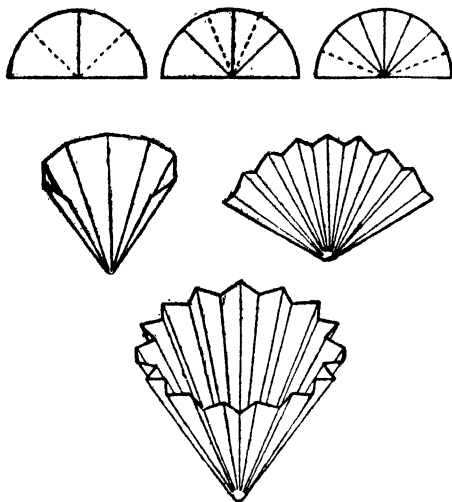


Fig. 5. Stages in making a fluted filter paper.

soon, even before the solution passes through the filter, the filtration should be done in small quantities and at intervals, the substance being kept in solution by constant heating.

**Crystallisation.** After filtration is over, the beaker containing the solution is covered with a clean watch glass and allowed to cool. Rapid cooling and vigorous stirring produce fine crystals which are more readily freed by suction from the mother liquor than large crystals. In the case of low-melting solids, the solution as well as the crystallisation processes are difficult operations. The solution should be made in a fairly large amount of the solvent and cooled very slowly. There is a tendency in the case of some solutions to supercool : crystallisation can be started in such cases by scratching the sides of the vessel with a glass rod or seeding with a tiny fragment of the crystal.

**Isolation of the crystals.** When the solution is quite cold and there is no further crystallisation, the crystals are filtered at the pump using the Buchner funnel, or Hirsch funnel, or an ordinary funnel with a Gooch filter disc (Fig. 6). The filter paper, cut circularly to the size of the filter disc, is placed in the

funnel, moistened with a few drops of the solvent and the crystals transferred along with the mother liquor to the filter, the residual

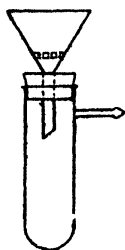


Fig. 6. Funnel with Gooch filter disc.



Disc.

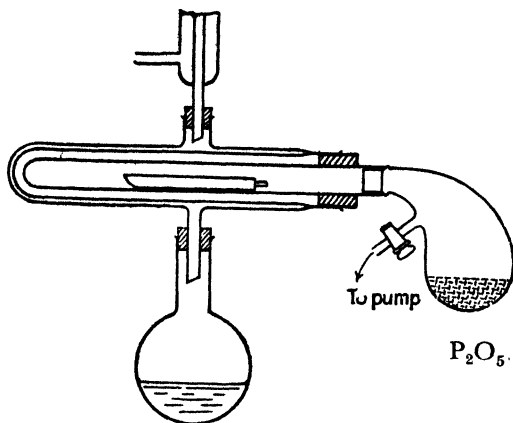


Fig. 7 (a). A proper solvent depending upon the m. p. of substance to be dried is taken in the flask.

solid in the beaker or flask being transferred by adding a few c.c. of the cold solvent. The crystals are washed with small amounts of the cold solvent once or twice. After most of the solvent has drained off, the crystals are pressed by a nickel spatula or a clean flat glass stopper, and any further adhering liquid is removed by suction for a few minutes. The crystals are then transferred to a porous plate, pressed firmly round the sides and left for air drying.

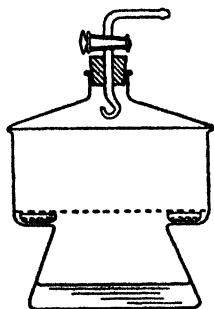


Fig. 7 (b)

Traces of moisture or solvent can sometimes be removed only by keeping the crystals in a vacuum desiccator Fig. 7 (b) over concentrated sulphuric acid (or any other suitable dehydrating agent) or by heating in a drying pistol, Fig. 7 (a).

**Expt. (1) Purification of acetanilide or ortho-chlorobenzoic acid (crude).** Weigh about 5 gms. of the impure compound into a 250 c.c. beaker. Add 50-60 c.c. of boiling water and by

vigorous stirring with a glass rod dissolve the material, adding small amounts of boiling water if necessary. When the material has dissolved in water leaving only mechanical impurities, add 1-2 gms. of animal charcoal (or "Norit") and boil for a further period of two minutes. Then filter through a hot water funnel containing a fluted filter paper pouring the hot solution in two or three portions and keeping the solution gently boiling all the time. Collect the filtrate in a clean beaker and while cooling stir frequently until no more crystals separate. When the solution is quite cold, filter the crystals on the Buchner funnel as described, wash with a small amount of cold water and press with a spatula or the flat end of a clean glass stopper. Dry the crystals on a porous plate and weigh when quite dry. Determine the melting point to see if the substance is quite pure. The melting point should not differ by more than  $1^{\circ}$ .

**Expt. (2)** Repeat the above experiment using benzoic acid or cinnamic acid and alcohol.

The cinnamic acid or benzoic acid is dissolved in the minimum amount of hot alcohol. Then hot water is added drop by drop till a precipitation of the acid just takes place even in the hot solution. The solution is heated till it becomes clear and then cooled. The crystals are filtered and dried exactly as described.

**Expt. (3)** Dissolve 1 gm. of meta-dinitrobenzene in the least amount of cold dry benzene. Then add ligroin in drops till the dinitrobenzene has separated more or less completely. The substance dissolves completely in benzene but is insoluble in ligroin or in mixtures of benzene and ligroin. Filter the crystals using a small funnel and a Gooch filter disc; wash the crystals with a little ligroin. Dry and determine the melting point.

**Fractional crystallisation.** When it is definitely known that a solid is a mixture of two substances a separation of the two can be attempted by fractional crystallisation from a solvent in which both are soluble but to different degrees. The solvent to be used has to be found out only by trial and unless there is an appreciable difference in the solubilities of the two compounds the process of separation becomes laborious. The mixture is shaken up with a suitable quantity of the solvent, hot or cold, so as to dissolve nearly the whole of the more soluble

part leaving the less soluble part undissolved. A small amount of the less soluble component also goes into solution. The solution is filtered even while hot and the more soluble part is obtained on cooling and concentrating the solution if necessary. The solid obtained is filtered, dissolved once again in the minimum amount of the solvent and recovered by crystallisation. This process of solution and crystallisation is repeated a number of times and in later stages the mother liquor of the previous filtration can be used as the solvent to prevent loss of material.

The residue after the first filtration consisting chiefly of the less soluble part, is worked up in a similar manner to get rid of the more soluble part. Each crop of crystals should be tested for purity by a melting point determination and for homogeneity by means of the microscope in cases where the two constituents show a well defined difference in crystal structures. The number of fractions obtained will vary with the nature of the substances in the mixture and the processes of solution and crystallisation are to be repeated till the fractions obtained consist of single substances. The relative solubilities of the two substances and the proportions in which they are present, are the deciding factors as to which of the two will separate first. If a very large quantity of the more soluble substance is present, it is quite possible that the first fraction consists of the more soluble part.

**Expt. (4) Separation of benzoic and cinnamic acids.**

An intimate mixture of 2 gms. of each is placed in a 100 c.c. beaker and warm water at 40° (50 c.c.) is added. The mixture is stirred with a thermometer and the temperature maintained at 40° for about five minutes by careful warming on a hot water bath. The contents of the beaker are allowed to settle and the supernatant liquid filtered hot, using a hot water funnel collecting the filtrate in a 400 c.c. beaker. The residue in the beaker is treated similarly six times with warm water and after each extraction will be getting richer in the less soluble cinnamic acid. The final residue is recrystallised from boiling water, filtered, dried on a porous plate and its melting point determined (133°). The combined filtrate containing all the benzoic acid is evaporated down to a bulk of 50. c.c.; on cooling, benzoic acid crystallises out. The acid is purified by recrystallisation and its melting point determined (121°).

	t = 30°	40°	50°	100°	
Solubility of benzoic acid					
in 100 parts of water	0.41	0.56	0.78	5.9	parts
„ of cinnamic acid in	0.055	—	—	1	parts
100 parts of water	(25°)				

Other common mixtures which can be separated by this process are :

(1) Benzoic and Benzilic acids, the latter being less soluble in hot water.

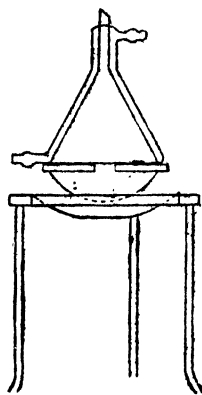
(2) Benzoic acid and Benzamide. Benzoic acid and Benzamide dissolve to the extent of 0.3 and 1.35 parts respectively in 100 parts of water at 25°.

(3) Salicylic acid and Phthalimide. Salicylic acid dissolves to the extent of 0.204 at 25° and 1.76 at 75° in 100 parts of water while only 0.06 part of Phthalimide dissolves at 25° in the same volume of water.

(4) Benzoic acid and  $\beta$ -Naphthol. This mixture is somewhat more tedious to separate.

**2. Sublimation.** Solids that have a high vapour pressure may be purified by the process of sublimation in which the solid passes into the vapour state without melting and by appropriate arrangements, the distilled vapour is condensed to form crystals.

A simple apparatus of sublimation is illustrated in fig. 8. The substance to be sublimed is placed in a porcelain basin about 12 cm. diameter, a circular asbestos board with a central hole, 3 cm. diameter cut in it, is placed in the dish, so that it rests at about the middle of the dish and a circular filter paper with a central hole covering the one on the asbestos board is placed on it. An inverted water jacketed glass funnel is placed over the paper and the stem of the funnel is plugged loosely with cotton or filter paper. The substance is heated on a sand bath. The vapour rises through the central hole and condenses in the hollow of the funnel and on the filter paper.



**Expt. (5)** Purify by sublimation naphthalene, camphor, anthraquinone ; use 4 gms. of each.

Fig. 8 Apparatus for sublimation



**Sublimation under reduced pressure.** Many substances which decompose on heating at ordinary pressure may often be

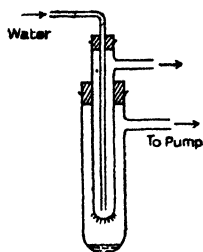


Fig. 9 (a)

The 'cold finger' is fitted into the larger tube by means of a rubber stopper.

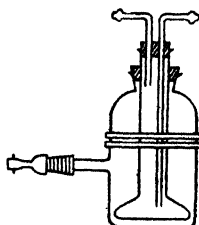


Fig. 9 (b)

Sublimation still for quantities up to 100 g.

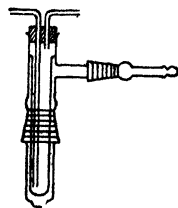


Fig. 9 (c)

All glass vacuum sublimation apparatus for quantities of a few m.gm. up to 1 g.

purified by sublimation under reduced pressure. A simple apparatus for the purpose is shown in Fig. 9. The impure substance is placed in the wider tube and the apparatus is exhausted. On heating gently, by immersion in an oil-bath, pure substance collects on the cold surface.

**3. Distillation.** This is the universal process applied for the purification of organic liquids. Four types of distillation are possible depending chiefly on the nature of the substance.

(a) *Simple distillation.* This is employed for the purification of an organic liquid associated with traces of impurities,

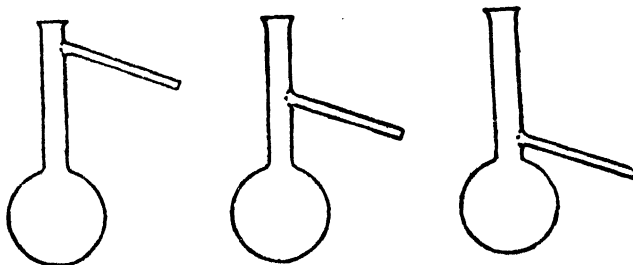


Fig. 10. Flasks for distillation.

non-volatile or volatile. The apparatus required is a simple distillation flask fitted with a cork carrying a thermometer, a suitable condensing device and a clean dry receiver. The capacity of the flask should be roughly three times the volume

of the liquid to be distilled. The position of the side-tube is another important factor. For liquids with a low boiling point the side-tube should be as high as possible and nearer the mouth, for liquids with a medium boiling point ( $100-150^{\circ}$ ) the side-tube should be at the centre and for high boiling liquids it should be as low as possible (Fig. 10). The flask should be fitted with a wooden cork, free from too many holes, carrying a thermometer the bulb of which should be just a little below the side-tube, so that the bulb of the thermometer is completely surrounded by the vapour. With a proper flask there should be little difficulty in reading the thermometer through obstruction by the cork carrying the thermometer.

The liquid is poured by means of a funnel into the distilling flask which is connected to a condenser by means of a cork.

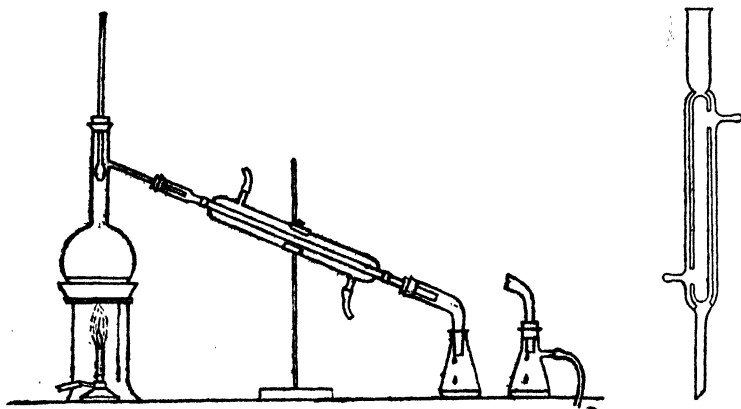


Fig. 11 (a). Apparatus for distillation with Liebig's condenser. Fig. 11 (b)

(Fig. 11a). An ordinary Liebig's condenser should be used for liquids boiling below  $140^{\circ}$ , a double surface condenser (Fig. 11b) is often used when the recovery is to be effective, while for liquids boiling above  $140^{\circ}$  an air condenser (Fig. 11c) should suffice. Before heating is commenced two or three small pieces of unglazed porcelain are placed in the flask to prevent bumping. Heating is done gently at first and then steadily till the temperature is constant and distillation is regular. The distillate is collected at this stage and the steady temperature noted as the boiling point of the liquid. The main fraction distilling within a range of

2-3°, should be collected separately. With inflammable liquids the receiver may as well be a dry Buchner flask attached to the condenser by means of a cork. Liquids which boil below 80° are

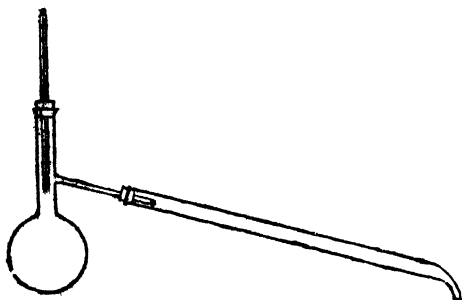


Fig. 11 (c). Flask fitted with an air condenser.

heated on a water-bath. In the case of liquids with high boiling points a naked rotating flame may be used.

(b) *Fractional distillation.* When the liquid consists of a mixture of two or more volatile components, it is distilled in fractions so as to recover all. A quantitative separation is rarely possible; fractional distillation using the ordinary distillation apparatus can be used to separate mixtures of two or more liquids when the boiling points of the components differ by at least 40°. A mixture of benzene (b.p. 80.2°) and nitrobenzene (b.p. 210.9°) is satisfactorily separated by distilling the mixture slowly collecting the distillates separately.

**Expt. (6) Purification of ethyl acetate.** The impurities present in ethyl acetate are chiefly acetic acid and ethyl alcohol. The ester (75 c.c.) is taken in a beaker and treated with a dilute solution of sodium carbonate with continuous stirring till the upper layer of the ester tested with litmus paper is no longer acid. The lower aqueous layer is removed and the upper layer shaken with a strong aqueous solution of calcium chloride (50%) to remove alcohol. The lower layer is again run off and the ester dried in the funnel by adding lumps of anhydrous calcium chloride and leaving over-night. The ester is filtered into a dry distilling flask through a fluted filter and distilled on the water-bath using a Liebig's condenser. The portion distilling between 76-78° is collected in a dry bottle.

**Expt. (7)** Into a 100 c.c. distilling flask place 25 c.c. of dry benzene and 25 c.c. of nitrobenzene. Fit the flask with

a good one-holed cork carrying a thermometer. Attach a short Liebig's condenser to the flask and distil the mixture by using a micro-burner. Collect the distillate coming over at first between  $78-82^{\circ}$  in a dry receiver and when the temperature rises to  $100^{\circ}$  replace the condenser by a short air-condenser, change the receiver and heat the flask directly with a small rotating flame; the temperature rises quickly to  $200^{\circ}$ , the liquid distilling from  $200^{\circ}$  to  $210^{\circ}$  being collected separately. Repeat this process carefully and the distillates obtained finally are pure benzene and nitrobenzene respectively, the separation being almost quantitative.

When the boiling points lie near each other, the separation cannot be easily accomplished by using a simple distillation apparatus, as the vapour passes too rapidly into the condenser. This difficulty is avoided by using a fractionating column. A number of fractionating columns are available all of which act on the same principle. The purpose of a fractionating column is to condense the vapour of the less volatile liquid which is carried along with the vapour of the more volatile liquid and to allow only the latter to pass into the distillate. A large cooling surface is offered to the rising vapours which are always in contact with the condensate. The more volatile portion of the condensate is revapourised by the ascending vapour and the less volatile portion of the vapour is condensed. Intimate contact between liquid and vapour is therefore necessary and this is achieved by spreading the liquid as a thin film by using glass beads or discs which offer obstruction, thus allowing the vapour to actually bubble through the condensate in each section.

**Expt. (8)** Separation of Benzene and Toluene or Carbon tetrachloride and Toluene by fractional distillation.

A 200 c.c. round-bottom flask is fitted with a simple fractionating column having two bulbs (Fig. 12a) or a Young's pear-shaped still head with four bulbs using a good wooden cork (Fig. 12c). If a simple fractionating column is used, the bulb portion should be completely filled with glass beads. A mixture of the two liquids to be separated (30 c.c. + 30 c.c.) is then introduced into the flask and a cork carrying a thermometer is fitted into the column, the side-tube of this being connected to a small Liebig's condenser. The flask is

covered with asbestos paper up to the side-tube of the column to prevent loss of heat by radiation. A few pieces of porous

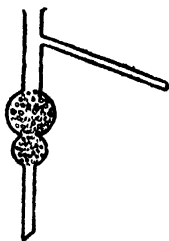


Fig. 12 (a)



Fig. 12 (b)

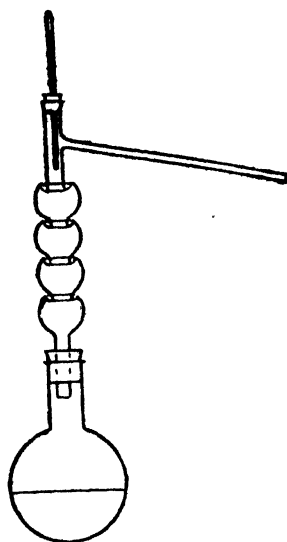


Fig. 12 (c)

porcelain are placed in the flask which is heated by a micro-burner, the heating being so regulated that the liquid distils slowly and regularly.

A number of test-tubes ( $6'' \times \frac{5}{8}''$ ) (six) should be labelled 1 to 6. The first fraction ( $80-85^\circ$ ) is collected in tube 1. When the temperature rises above  $85^\circ$ , the second fraction is collected between  $85-90^\circ$  in tube 2 and the other fractions between  $90-100^\circ$ ,  $100-105^\circ$ ,  $105-111^\circ$ . The remainder of liquid constitutes the residue principally of toluene and ordinarily will be very small in amount being that necessary to wet the surface of the apparatus. This residue, after cooling the apparatus completely, is poured into the last tube.

The distillation is repeated commencing with fraction 1. The portion coming over between  $80-85^\circ$  is collected in tube (1). When the temperature passes this stage, fraction (2) is added and distillation continued, the portion boiling over between  $80-85^\circ$  being collected in the tube 1. This procedure is continued in the same manner, with addition of the 2nd, 3rd, 4th, 5th, fractions one after the other and collecting the fractions over the same range. The final distillation is effected

by redistilling the first and last fractions separately, collecting the distillate between 80-82° in the one case and between 108-110° in the other. The residue, if considerable, may be added to the higher boiling fraction during the redistillation.

The volume of each of the fractions is measured (*vide* table) and the ratio of the volume obtained to the volume taken in each case calculated so as to give an idea of the amount of each liquid that can be recovered by the process.

In the case of a mixture of two liquids belonging to a homologous series (Benzene and Toluene), fractional distillation is more difficult than in the case of a mixture of carbon tetrachloride and toluene which belong to different chemical types.

B.P. range.	Fraction	1st Distillation. Volume in c.c.	2nd Distillation. Volume in c.c.	3rd Distillation. Volume in c.c.	4th Distillation. Volume in c.c.	5th Distillation. Volume in c.c.	Total Volume
80—85°	I						
85—90°	II						
90—100°	III						
100—105°	IV						
105—111°	V						

**Azeotropic mixtures.** Liquids differing widely in their boiling points are often found to form mixtures of a definite composition having a constant boiling point at constant pressure, usually that of the atmosphere. These liquid mixtures behave like pure liquids with boiling points which may be below or above that of either component and cannot be separated into their constituents by fractional distillation. They are called azeotropic mixtures. When the system contains two components, it is called a binary system. As examples, we have acetone and chloroform forming a mixture with a maximum boiling point, while ethyl alcohol and benzene, and methyl alcohol and chloroform form minimum boiling mixtures.

**Expt. (9) Variation of vapour pressure (boiling point) with composition in a two component system.** A 250 c.c. bolt-necked flask is closed with a two holed cork carrying a vertically fitted Liebig's condenser and a thermometer the bulb of which is dipping into the liquid. The flask with the condenser (Fig. 13) is placed on a square piece of a thick asbestos board

with a central hole supported on a tripod stand and the condenser is fixed in a clamp at an inclination of about  $45^\circ$  to the vertical.

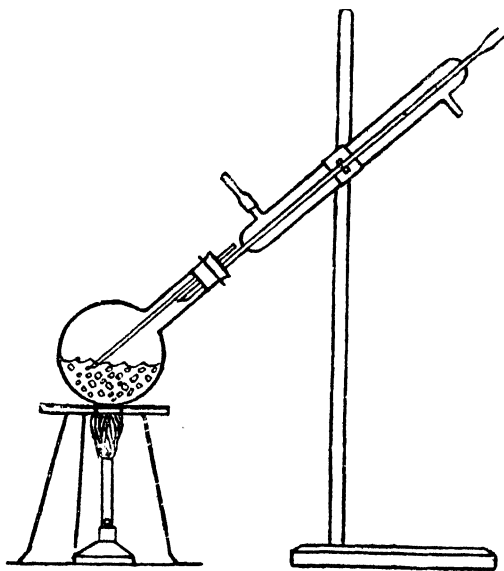


Fig. 13. Apparatus for study of azeotropic mixtures.

30 c.c. of chloroform are introduced by a pipette into the flask, one or two pieces of porous porcelain are dropped in, the flask heated with a microburner and the boiling point of the pure liquid determined when the liquid is condensing freely and the thermometer is steady. The burner is removed, the liquid cooled and 2 c.c. of acetone added through the condenser so that it falls directly into the flask. The boiling point of the mixture is then determined as before. In this manner acetone is added in lots of 2 c.c. at first, then in lots of 5 c.c. When the rise in the boiling point is not marked, addition may be made in lots of 10 c.c. also. At least ten readings should be taken. The experiment is repeated starting with acetone in the flask and adding chloroform in successive steps as before. The readings are tabulated as shown below and a curve is constructed with temperature as the ordinate and composition as the abscissa. The maximum temperature is taken as the boiling point of the mixture for the corresponding composition.

A = chloroform, density at 30° = 1.4700.

B = acetone, " " = 0.7784.

Vol. of liq. A.	Vol. of liq. B.	Wt. of liq. A.	Wt. of liq. B.	Percentage		B.P.
				A.	B.	
30 c.c.	0 c.c.	44.10 gms.	0 gms.	100	0	61.6°
"	2	"	1.557	96.56	3.44	62.3
"	4	"	3.114	93.4	6.60	63.3
"	6	"	4.670	90.4	9.60	63.7
"	8	"	6.227	87.6	12.40	64.1
"	10	"	7.784	85.0	15.00	64.6
"	15	"	11.676	79.05	20.95	64.8
"	20	"	15.568	73.92	26.08	64.7
"	30	"	23.352	65.37	34.63	64.2
"	40	"	31.136	58.60	41.40	63.3
"	30	0	23.352	0	100	57.0
2	"	2.94	"	11.2	88.80	58.0
4	"	5.88	"	19.93	80.07	59.0
6	"	8.82	"	27.44	72.56	59.7
8	"	11.76	"	33.50	66.50	60.7
10	"	14.70	"	38.63	61.37	61.1
15	"	22.05	"	48.58	51.42	62.3
20	"	29.40	"	55.73	44.27	63.2
30	"	44.10	"	65.39	34.61	64.1
40	"	58.80	"	71.57	28.43	64.6
50	"	73.50	"	75.89	24.11	64.7
60	"	88.20	"	79.07	20.93	64.8

The maximum boiling point and the composition may be computed from the curve (Fig. 14) given below :

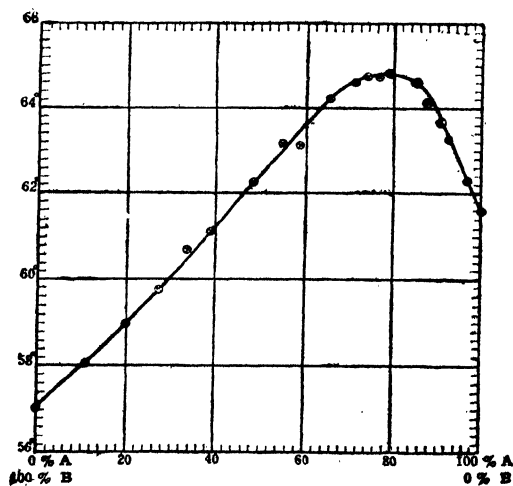


Fig. 14. Constant boiling mixture with a maximum boiling point.

A = Chloroform, B = Acetone.



## Binary azeotropic mixtures :—

Substance	B.P.	Density at 30°	Substance	B.P.	Density at 30°	Percentage by wt. of A.	Percentage by wt. of B.	Boiling point of mixture.
Chloroform	61.2	1.47	Acetone	56.4	.79	79.5	20.5	64.6 (maximum)
Chloroform	„	„	Methyl alcohol	61.6	.79	87.5	12.5	53.5 (minimum)
Ethyl alcohol	78.3	0.79	Benzene	80.8	.88	31.5	68.5	66.9 (minimum)

(c) **Distillation under reduced pressure.** This process of purification is applicable to liquids which boil at a very high temperature and show a tendency to decompose when distilled under ordinary atmospheric pressure. Low melting solids, or liquids which undergo oxidation during distillation at atmospheric pressure, can also be distilled under diminished pressure without any decomposition taking place. The temperature at which a substance boils is markedly lowered by a decrease in pressure. For example, benzophenone boils at 360° at 760 mm. pressure, and at 170° under a pressure of 15 mm., or glycerol which boils at 290° with decomposition at atmospheric pressure, distils without decomposition at 180° under 12 mm. pressure.

The requisites for carrying out this distillation are :—

- (1) a distillation flask, preferably of the Claisen type, provided with two necks,
- (2) a receiver which may also be a simple distillation flask,
- (3) a wide-mouthed safety bottle (fitted with a three-holed bung and having a capacity of nearly one litre),
- (4) a good water pump or motor-driven oil pump like the Gaede pump and a manometer. Under ordinary conditions a water pump is capable of evacuating a small system to a pressure of about 40 mm. at 30°, the minimum pressure being determined

by the vapour pressure of the water passing through it. Pressures under 1 mm. are reached with a mechanical oil pump.

**Expt. (10) Purification of Ethyl aceto-acetate.** Commercial ethyl aceto-acetate contains acetic acid and ethyl acetate as impurities. The ester, about 50 c.c., is placed in a separating funnel, washed with a small amount of saturated sodium bicarbonate solution to remove acetic acid, then with water and finally dried over anhydrous magnesium sulphate or potassium carbonate.

The ester is filtered into a Claisen flask of nearly four times the capacity through a fluted filter paper. The longer neck of the Claisen flask is fitted with a good cork free from holes carrying a glass tubing 5-6 mm. diameter drawn out at one end into a fine capillary. The capillary should be flexible and deliver very minute bubbles and reach exactly to the bottom of the flask. A rubber tube and pinch-cock are placed on the wider end of the tube projecting out of the cork. The shorter neck of the Claisen flask which acts as a small fractionating column is fitted with a thermometer. The purpose of the capillary thread is to keep up a steady ebullition and prevent bumping by drawing a continuous current of air or an inert gas if necessary. The Claisen flask minimises the chance of mechanical contamination of the distillate from frothing or violent bumping both of which are common in vacuum distillation. The side-tube of the Claisen flask is connected to a simple distillation flask by a rubber stopper and should reach the centre of the bulb of the receiver. Two or three of these flasks, thoroughly dried, are kept ready especially when changing receivers for purposes of collecting fractions and the necks of these should be of the same dimensions. The receiver is cooled by a stream of cold water and the waste water is carried away by means of a large funnel on which the receiver rests. The side-tube of the receiver is connected to a safety flask by pressure tubing (1-2 mm. bore). The safety flask or bottle is fitted with a three-holed stopper for connection to the suction pump, manometer, and a stop-cock for diminishing the vacuum before disconnecting.

Before carrying out the distillation the assembled apparatus (Fig. 15) is to be tested for air-tightness, the liquid to be distilled being placed in the flask after this preliminary trial. Any leaks in the corks can be stopped by coating them with paraffin or Faraday's wax or collodion. The vacuum yielded by the pump is also determined by turning on the water pump to the full; this is

important in the matter of collection of the pure liquid whose boiling point changes with pressure. The boiling point of ethyl

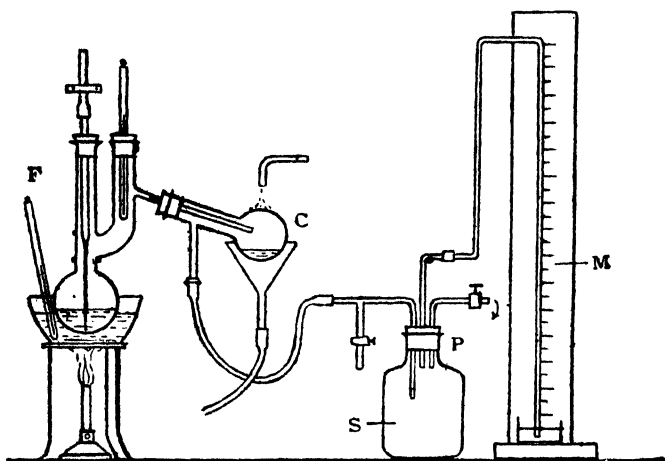


Fig. 15. Distillation under reduced pressure.

F. Claisen flask, C. cooling device, S. safety bottle, M. manometer,  
P. to pump.

aceto-acetate under the pressure yielded by the pump is read off from a curve, data for which are given below :

Pressure.	Boiling Point.
760 mm.	... 180°
80 "	... 100°
60 "	... 97°
30 "	... 88°
18 "	... 78°
14 "	... 74°
12 "	... 71°

The Claisen flask is heated in an oil or glycerol bath, or a bath of Wood's fusible alloy, the temperature of the bath being always maintained about twenty degrees higher than that of the distilling vapour. The heating of the bath is begun only after the vacuum has been produced. At first ethyl acetate distils over and when under the recorded pressure of the system the boiling point approaches that of the ethyl aceto-acetate, the receiver is changed. This is done by cooling the system slightly and releasing the vacuum by opening the stop cock, before shutting off the water pump (if it

be used), to prevent back suction of water. A fresh receiver is attached and the pure ethyl aceto-acetate collected over a range of 5-6°.

### Fractional distillation under diminished pressure.

It is necessary sometimes to collect the distillate in a series of separate fractions. This may be done without interrupting the distillation in vacuum by the use of the Geissler's triangular receiver, also known as Perkin's triangle (Fig. 16). The Claisen flask is attached either directly to the triangular receiver or through a short Liebig's condenser as shown in the figure. A and B are two-way cocks and C a three-way cock. While a fraction is being collected in R, B and C are closed and A is open. The liquid in R is drawn into S by closing A and opening B and C, connection being established between S and the pump through C. Then A and B are closed, air admitted through C and the receiver S is changed. The new receiver is now evacuated and the whole process repeated without interrupting the vacuum.

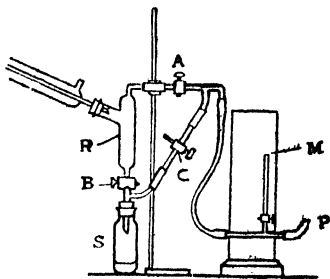


Fig. 16. Fractional distillation under reduced pressure. Perkin's triangle. M. Manometer, P. To Pump.

(d) **Steam Distillation.** Many substances which are volatile with decomposition or which are not easily volatile, show a tendency to volatilise in a current of steam. To test for volatility in steam, heat a small amount of the substance with a little water in a test tube to boiling and hold the bottom of a second test tube containing ice in the issuing vapours until a drop of water has condensed on the cold surface. If the drop is turbid it indicates that the substance is volatile in steam. The recovery of such substances by volatilisation with steam is facilitated when they are practically immiscible with water and are not decomposed by steam. This method is only applicable to substances which have an appreciable vapour pressure in the neighbourhood of 100°. The vapour pressure of such a system is the sum of the vapour pressures of the two components and the boiling point of the mixture is below the boiling point of either component. Thus it is possible to effect the separation of a high boiling liquid by steam distillation alone, without resorting to distillation in vacuum. This process is used

for the purification of organic substances such as aniline, bromobenzene etc., and also for the isolation of various essential oils of plants. The advantages of steam distillation will be evident from the following example :

Nitrobenzene and water form a pair of liquids usually called immiscible. The boiling point of the former is  $210.9^{\circ}$  at 760 mm. and of the latter  $100^{\circ}$ . The mixture of these two boils under 760 mm. at  $99^{\circ}$ .

Vapour pressure of the mixture = Vapour pressure of water  
+ vapour pressure of nitrobenzene.

$$760 \text{ mm.} = 733(\text{at } 99^{\circ}) + 27 (99^{\circ})$$

Since the molecular weights of water vapour and nitrobenzene are 18 and 123, the weight relationship of the two will be as  $\frac{18 \times 733}{760} : \frac{123 \times 27}{760} = 4 : 1$  nearly. The smaller vapour pressure of the nitrobenzene is thus compensated by its higher molecular weight. This process is also applicable to the separation of solid mixtures when one of the components has an appreciable vapour pressure at  $100^{\circ}$  (mixture of o- and p-nitrophenols).

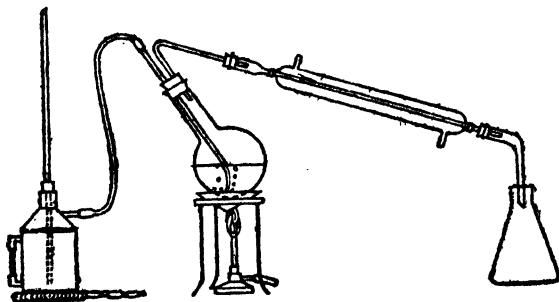


Fig. 17. Steam distillation.

The apparatus (Fig. 17) consists of a steam generator—a tin can or copper can with a water gauge and fitted with a two-holed cork carrying a long tube as a safety tube and a delivery tube leading to a distillation flask. The latter may be a litre round-bottom flask fitted with a two-holed rubber stopper carrying a long bent tube for delivery of steam and a short one for outlet of vapour, connected to a Liebig's condenser. The flask is to be filled with the liquid to not more than half its capacity and is preliminarily heated to prevent condensation of steam. A receiver is

attached to the condenser for collecting the distillate which is a mixture of water and the substance volatilising over.

Separate by steam distillation the following mixtures :—

**Expt. (11-a)** p-dichlorobenzene and salicylic acid or o-nitrophenol and p-nitrophenol.

Mix about 5 g. of each thoroughly in a mortar and transfer the mixture to a steam distillation flask, add about 50 c.c. of water and distil with steam. When no more solid passes over, stop the current of steam, disconnect the distillation flask, filter hot through a fluted filter (before cooling), concentrate the solution and set aside to crystallise (salicylic acid or p-nitrophenol). Separate the solid material in the distillate by filtering, press the solid with a spatula to free from adhering liquid and dry on a porous plate. If the substance solidifies in the condensing tube, the water in the outer jacket is let off momentarily when the heat from the vapour melts the crystals.

The filtrate from the distillation flask deposits crystals on cooling or sometimes only on concentration. The crystals are separated by filtration and the weight and m.p. of each component of the mixture is determined.

**Expt. (11-b) Aniline and Nitro-benzene.** Take about 10-15 g. of the given mixture in the round-bottom flask, add 50 c.c. of water and about 25 c.c. of concentrated hydrochloric acid and distil in steam. The aniline forms the hydrochloride whose vapour pressure is negligible. Collect the disillate consisting of nitro-benzene and water in a receiver. When no more nitrobenzene distils, as can be seen from the oily drops ceasing to pass over, stop the distillation, cool and add a slight excess of a strong solution of sodium hydroxide to the residual liquid. Aniline is liberated and is separated by distilling in steam once again, the distillate being collected in a separate receiver.

The first distillate containing nitrobenzene is transferred to a separating funnel and the lower layer of nitrobenzene is separated and dried over anhydrous calcium chloride. The liquid is purified by distillation, the distillate collected in a weighed tube and the weight of nitrobenzene recovered determined. The distillate should be collected between 202-210°. The boiling point of nitrobenzene is 210.9° and its density, 1.208.

The second distillate consists of aniline which sinks, being slightly heavier than water. The lower layer of aniline is tapped off and kept in the separating funnel over solid sodium or potassium hydroxide, allowing the liquid to stand for an hour or two. The liquid, thus dried is distilled as usual collecting the distillate between  $180-184^{\circ}$ ; boiling point,  $182^{\circ}$  and density, 1.027. Owing to the solubility of aniline in water some aniline is lost in the upper aqueous layer. Complete recovery of the aniline is made by the process of salting out and extraction with a suitable solvent (chloroform).

A mixture of aniline and phenol can be separated as above by steam distilling in alkaline solution, when phenol is kept back and aniline passes over first. Afterwards the solution is rendered acid with hydrochloric acid to congo-red paper and steam distilled once again to recover the phenol.

**Distillation with superheated steam.** Substances which volatilise only with great difficulty are best recovered by

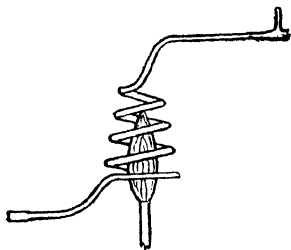


Fig. 18 (a) Superheater.

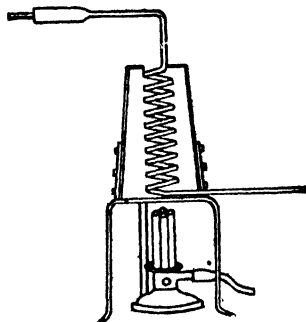


Fig. 18 (b) Lassar-Cohn's steam drier.

distillation with superheated steam. The superheating takes place either in the copper tube wound in a conical spiral (Fig. 18 a) or in a Lassar-Cohn's steam-drier (Fig. 18 b) which is interposed between the steam generator and the flask and heated from below with a burner. The flask with the substance is placed in an oil bath heated to a temperature of about  $150^{\circ}$ .

**4. Extraction with solvents.** The aniline and phenol recovered from the mixture by steam distillation are both appre-

ciably soluble in water. A certain amount of ether will therefore be inevitably lost unless recovered by extraction with a suitable solvent in which the aniline or phenol is more soluble than in water. Ether is the solvent almost invariably used for recovery of substances which are soluble in water. In general any solvent used should be practically immiscible with water. Actually no two solvents are absolutely immiscible but each is slightly soluble in the other. Ether, however, is more soluble in water than other solvents (8.1% at 15°). The general principle of this extraction process is that in dilute solutions a substance distributes itself between two immiscible or slightly miscible solvents in such a manner that the ratio of its concentration in one solvent to that in the second solvent is constant provided the temperature is constant and effects such as association or dissociation of the dissolved substances do not occur. This constant is known as the distribution co-efficient or partition co-efficient. For extraction, it is always advantageous to use a given volume of solvent in two or three lots whereby the maximum amount of the dissolved substance can be recovered from solution rather than to use the whole in one lot.

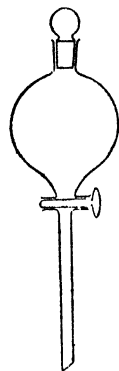


Fig. 19  
Separating Funnel

In the case of aqueous solutions the solubility of the dissolved substance is diminished by the presence of dissolved inorganic salts. Alcohol which is completely miscible with water separates out when the aqueous solution is saturated with potassium carbonate. Sodium chloride is another substance used for the same purpose. This is known as the salting-out effect.

**Expt. (12)** The aqueous distillate in the previous experiment (11-b) amounting to 250 c.c. nearly, is first saturated with common salt and the liquid transferred to a separating funnel (Fig. 19) with a capacity of 500 c.c.; 100 c.c. of ether are then added and the funnel closed by the glass stopper or a tight fitting cork and shaken vigorously. The stem of the funnel is inclined upwards and the pressure released by gradually opening the stop-cock. The stop-cock is closed and the funnel supported on a ring and the liquid allowed to separate into layers. The lower aqueous layer is withdrawn into a beaker and the upper ether layer poured into a



**flask.** The aqueous layer is once again transferred to the separating funnel and the extraction repeated twice or thrice using 50 c.c. ether each time. If the ether layer does not separate easily or if an emulsion is formed, agitation with a glass rod or the addition of a few drops of alcohol facilitates the separation of the ethereal layer.

The combined ether extract is transferred to the separating funnel and dried over a suitable drying agent as water is soluble to some extent in ether. For aniline, pellets of sodium hydroxide are used and for phenol anhydrous sodium sulphate or magnesium sulphate can be used, the latter being preferable in our climates. Enough of the drying agent is added and the extract shaken twice or thrice to obtain a clear liquid. It is desirable to leave the extract after shaking, over the drying agent, for about half an hour. The ether extract is then filtered into a dry distilling flask of about twice the capacity, a few pieces of porous porcelain are added and the ether distilled off on a hot water bath. The residue is purified by distillation as usual.

**Drying of solutions.** When a substance has been extracted from an aqueous solution with an organic solvent, its solution is saturated with water and must therefore be dried. In the choice of drying agents, it should be borne in mind that the drying agent, while being insoluble in the solvent, should not react either with the solvent or with the solute. The most commonly used drying agent is granulated or fused calcium chloride. The drying agents to be employed in specific cases are given below :

**Common drying agents for organic compounds**

Anhydrous substance	Applicable to	Not applicable to	Drying power
Calcium chloride	Hydrocarbons, ethers, esters	Hydroxy and amino compounds	High below 30°
Calcium sulphate (Drierite)	All compounds	None	Low
Magnesium sulphate	All compounds	None	High
Potassium carbonate	Amines, alcohols, ketones	Acids	Medium
Potassium hydroxide	Amines, hydrazines, saturated hydrocarbons	Most compounds	High
Phosphorus pentoxide	Halides, hydrocarbons, nitriles	Most compounds	High
Sodium hydroxide	Amines, hydrazines, saturated hydrocarbons	Most compounds	High
Sodium metal	Ethers, saturated hydrocarbons	Most compounds	High

**Extraction of solid mixtures.** A solid mixture consisting usually of an inorganic substance with an organic substance is advantageously separated by the use of the Soxhlet extraction apparatus (Fig. 20).

The advantage of this process lies in the fact that a minimum amount of the solvent can be used without any wastage. The solvent is placed in a flask (A) attached to the Soxhlet tube (B) to which a short efficient condenser (C) is fitted. The solid is placed in a thimble made of hardened filter paper (D). At the top of the thimble a loose plug of cotton wool is placed to prevent any solid particles from being mechanically carried through. After assembling the apparatus, 100 c.c. of the solvent are placed in the flask along with a few glass capillaries to prevent bumping and the flask is then heated. The vapour rises through the side tube, as shown, is condensed and drops into the thimble and when it is full and reaches the top of thinner side tube (E), the liquid automatically siphons back into the flask with the extracted matter. The process is continuous. The substance being non-volatile, the extraction is carried out by the condensed liquid and a minimum amount of the solvent suffices for the extraction.

The extraction is usually complete after an hour or two of continuous operation and the substance can then be obtained pure by crystallisation from the solution. If the substance does not crystallize readily on cooling, the solution may be concentrated by distilling off a little of the solvent. Oils from oil bearing seeds such as castor seed, can also be extracted with the Soxhlet, using ether or ligroin as solvent. The seeds must be crushed, placed in the extractor over a little cotton wad and the operation carried out as described.

**Expt. (13)** Mix together 18 g. of potassium sulphate and about 6 g. of urea intimately and place in the thimble of the Soxhlet extractor. Place about 50 c.c. of absolute alcohol in the flask and carry on the extraction as described. Distil off the alcohol till the volume is 30 c.c. On cooling,

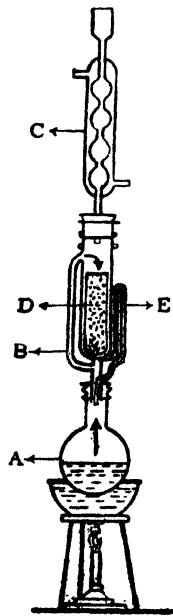


Fig. 20 Soxhlet extractor.

the crystals of urea which separate are filtered and dried. A second crop of crystals can be obtained from the mother liquor.

Determine the m.p. of the urea ( $132^{\circ}$ ).

### Chromatographic analysis

Even closely related substances possess different adsorption affinities for certain finely divided solids. Different adsorption affinities cause the components of a mixture of substances to move down a column of adsorbent at different rates when washed by a solvent. This is the principle employed in chromatographic analysis, a powerful method for the purification of substances.

### Apparatus

The apparatus employed for chromatography is very simple and may easily be improvised. Some of the general forms of apparatus are shown in figures.



Fig. 21 (a)

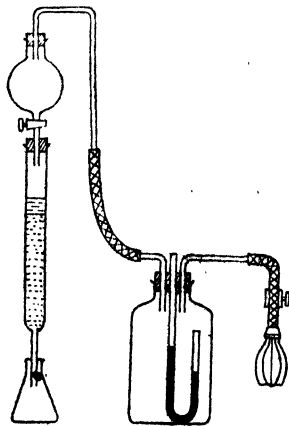


Fig. 21 (b)

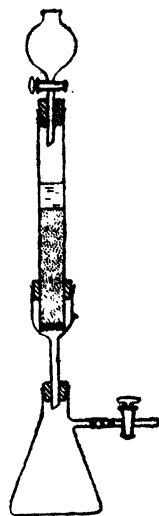


Fig. 21 (c)

In Fig. 21 (a), the tube bears on its lower end a ground glass joint by which it is attached to an adapter fitted with a perforated glass plate or porous glass disc for supporting the adsorbent column. The solution is run through the column with gentle suction. In

Fig. 21 (b) an arrangement suitable for carrying out the operation under positive pressure is depicted.

In operations in which the zones are successively eluted into the filtrate (liquid chromatogram), an ordinary burette with a plug of cotton supporting the adsorbent is the simplest arrangement. Fig. 21 (c).

### Adsorbent

Activated alumina, the commonest adsorbent is commercially available in forms suitable for chromatographic analysis, and is employed in the case of neutral and basic substances. Silica gel is suitable for chromatography of acidic substances. Magnesium oxide, magnesium sulphate, magnesium carbonate, calcium hydroxide, calcium carbonate, glucose, lactose etc. are some of the other adsorbents employed. In general practice, about twenty to thirty times the weight of adsorbent is employed in relation to the mixture to be chromatographed.

### Preparation of the adsorbent column

Satisfactory results can be obtained only if the tube is packed uniformly with the adsorbent. This may be done by one of several procedures.

(a) The necessary support for the column (cotton wool or sintered or perforated glass plate) is placed in the tube which is clamped vertically. The adsorbent is added in portions. The first portion should be twice the size of those that follow. The individual portions are pressed down with a flattened glass rod or a cylindrical wooden pestle in the case of tubes wider than 1 cm. in diameter. From 1/5th to 1/3rd of the tube should be left empty.

(b) The adsorbent and solvent are placed in a separating funnel fitted with an efficient stirrer and the resulting slurry is allowed to flow into the clean dry tube. The adsorbent settles under force of gravity and a compact packing is obtained.

(c) A burette or glass tube provided with a tap tube is filled about half with the solvent. A plug of cotton is pressed down through the solvent to the bottom with the aid of a glass-rod. The adsorbent is added in small portions allowing it to settle down each time by gravity. The solvent is allowed to flow off until only a thin layer about 3 to 5 mm. is left over the adsorbent column. The top of the column should never be allowed to get dry.

## Solvents

The solvent employed in chromatographic work must be of the utmost purity. Solvents commonly employed are light petroleum (b.p. below  $80^{\circ}$ ) hexane, benzene, chloroform, ether, acetone, ethyl alcohol and acetic acid. An adsorbate usually adheres to any one adsorbent more firmly in a less polar solvent. The development of the column is often accomplished by changing over to a more polar solvent. Most adsorbates are broken up by methyl or ethyl alcohol. The addition of these in 0.5 to 0.2 per cent to the solvent is adequate for the purpose.

## Operation

A solution of the mixture in a suitable solvent is poured carefully on to the top of the column without disturbing the top layer of adsorbent. When the solution has almost drained, pure solvent is added and the development is commenced. In the case of coloured substances, the separation is followed visually by the formation of coloured bands. When the bands are sufficiently well separated, development is stopped, the column allowed to drain completely, pushed out of the tube with the wooden pestle, and the zones cut with a knife or scalpel. The adsorbates on the individual zones are eluted by use of a suitable solvent and the material recovered by evaporation of the solvent after filtration of the adsorbent.

In the case of colourless substances, the zones can in some cases be located by viewing in ultra-violet light. A generally applicable procedure for colourless substances is the liquid chromatogram method in which the column after adsorption is washed with a solvent or with a succession of solvents having increasingly powerful eluent action. The eluates are collected in arbitrary fractions and examined individually.

### Expt. (14) Separation of o-, m-, and p-nitranilines

A light petroleum solution of a mixture of the three nitranilines (0.15 g. of each) is poured on to a column of calcium hydroxide and the chromatogram is developed with light petroleum.

*Top* : light yellow, contains p-nitraniline.

*Middle* : yellow, m-nitraniline.

*Bottom* : dark yellow to brownish ; o-nitraniline. The compounds are isolated by elution of the zones with benzene containing methyl alcohol and removal of the solvent.

## CHAPTER II

### MANIPULATION OF SMALL QUANTITIES OF SUBSTANCES

In the qualitative analysis of organic substances the material available is most often of the order of 2 to 3 grams. With this quantity one has to carry out tests for the elements present, group or classification reactions, a melting or boiling point determination and finally the preparation of a suitable derivative using at least a decigram of the substance. No analysis can be regarded complete unless a derivative, preferably a solid, is prepared possessing a definite melting point easily verifiable from available literature. It is evident therefore that small quantities, at times of the order of milligrams, have to be employed for the different tests. Analytical methods involving the use of small quantities are usually called micro-methods. Economy of materials (in the shape of reagent) and economy of time are the two principal advantages attained in employing micro-methods. A thorough acquaintance with the technique of dealing with minute quantities is thus a most important part of a sound training in organic analytical work.

**Apparatus and methods.** The apparatus required for work of this type is very simple, and may be made easily whenever required. The type of apparatus to be used depends on the quantities employed for carrying out the reactions, apparatus of the dimensions noted below being sufficient for quantities up to a decigram :—

Test-tubes,  $4" \times \frac{1}{2}"$  ;

Test-tubes with side-tubes,  $4" \times \frac{1}{2}"$ , to serve as distillation tubes or as filtering tubes ;

Distillation flasks of 5 c.c. capacity ;

Small funnels, 2 cm. diameter ;

Filter papers, 2-3 cm. diameter.

When only milligram quantities are to be employed test tubes 3" long with a capacity of about 1 c.c. made from a 6 mm. glass tube are more suitable. A number of these, cleaned and dried, should be kept ready. When the closed ends of the tubes are drawn out to a conical shape they may be used in centrifuge

tubes to settle a small amount of a precipitate and to wash it before filtering. Crystallisation is carried out in a microbeaker which may be made from a test tube ( $3'' \times \frac{1}{2}''$ ) by heating the closed end to softening and lightly pressing it on a block of compressed charcoal.

Liquid reagents are delivered from pipettes 8 cm. long made from glass tubes of 3-4 mm. in diameter by drawing out one of the ends to a narrow bore. When regulated amounts of liquid reagents are to be added, the pipettes should be made from thermometer tubing or broken thermometers.

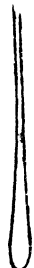


Fig. 22(a)



Fig. 22 (b). Micro-beaker and simple filter for crystallisation.

A micro-spatula (Fig. 22a) with a spoon end is indispensable. It is useful for a variety of purposes such as pressing a solid during filtration to free it from adhering liquid, adding small quantities of solid reagents etc. It can be made easily from a stout nickel wire, 4" long and 2 to 3 mm. diameter, by flattening one of the ends with a hammer, and making a depression in the flattened part so as to give it the shape of a tiny spoon. The other end is also hammered and flattened to give it the shape of a spatula. With this equipment it is possible to carry out without any inconvenience all the common processes of purification.

Heating of test tubes and centrifuge cones is always carried out in a suitable bath, since by open heating, as over a micro-burner, the liquid is easily thrown out.

**Expt. (15) Crystallisation.** About 0.05 to 0.1 g. of acetanilide is taken in a microbeaker, nearly boiling water is added in drops, using a glass pipette, till the substance dissolves completely. The beaker is heated carefully on asbestos-centred wire-gauze till it boils and the liquid is filtered through a micro-funnel made by drawing an ordinary test tube of  $6'' \times \frac{5}{8}''$  size at about one-third of its length from the mouth. The stem of the funnel is short and a small bulb is blown just near the narrow part. A loose plug of asbestos or cotton is placed in the bulb. The filtrate is caught in a micro beaker (Fig. 22b) and allowed to cool. If crystallisation does not take place, the beaker is thoroughly shaken closing with

the thumb. When crystallisation is complete the liquid is filtered through a 2 cm. funnel, fitted into a test-tube with side tube which serves as a filtering tube. A flattened thin glass rod (Fig. 23) hanging loosely serves as a filter plate and a piece of filter paper cut slightly bigger than the disc is placed over it. The liquid is poured on to the filter along a thin glass rod so that the precipitate collects at the centre and can be heaped to a mound for easy withdrawal later. After the adhering liquid has drained away, the glass rod is pushed and the filter paper with the precipitate is pressed on the porous plate for drying and determination of melting point.

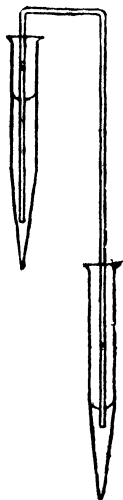


Fig. 24. Removal of a liquid by a capillary siphon.

capillary and automatically siphons away. When the liquid has drained off, the precipitate is stirred with a clean wire, a few drops of the cold solvent are added, and the mixture is stirred and centrifuged. The washing may be repeated, if necessary and the precipitate finally transferred directly to the porous plate without filtering. Crystallisation should be induced by shaking the tube, since substances frequently show a tendency to form super-saturated solutions.

The filtration of precipitates when

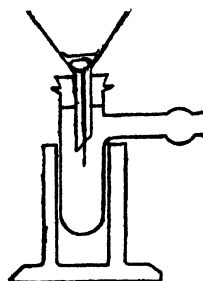


Fig. 23. Filtration on micro-scale.

If the precipitate in an experiment is very small originally, the solution for crystallisation is directly filtered into the centrifuge cone, cooled and then centrifuged so that the precipitate collects in the narrow end leaving the clear solution above. This solution can be siphoned off by a thin capillary bent into an L (Fig. 24). The shorter limb is gradually lowered into the centrifuge tube till the liquid rises through the

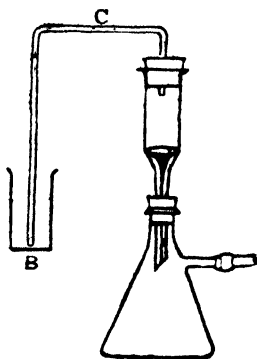


Fig. 25. Filtration of very minute quantities.



in small quantities is also accomplished by transferring the precipitate on to the filter through a siphoning arrangement (Fig. 25).

The precipitate contained in the tube B is transferred through the siphon C made by bending a glass tube of 3-4 mm. twice at right angles, to a small tube of the Allihn pattern in which a thin flattened glass rod is kept in the place of a filter disc. A piece of filter paper cut to shape is placed over the filter plate and suction applied by means of a pump. By gently rotating the tube, the precipitate can be completely transferred to the filter plate. It can also be washed in the same way by adding a few drops of the solvent to the tube which contained the precipitate and rotating it so that any remnants of the precipitate are similarly carried over. After suction for a few seconds, it can be dried on a porous plate as described.

**Distillation.** Distillation can be carried out in small distillation flasks of 5 c.c. capacity or using test-tubes with side-tubes in place of distilling flasks (Fig. 26*a*). Even fairly volatile liquids can be condensed by surrounding the receiver with ice water.

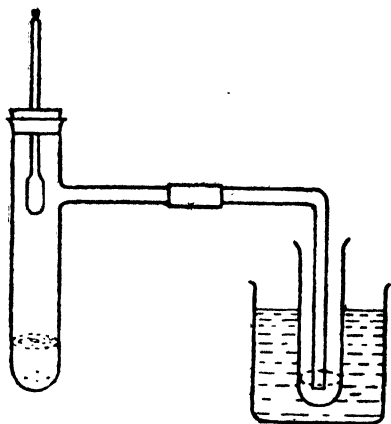


Fig. 26 (a). Simple distillation of small quantities of liquids.

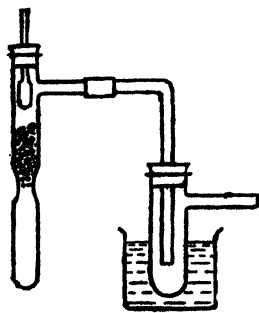


Fig. 26 (b). Fractional distillation of small quantities of liquids.

Effective fractionation of a mixture of two liquids is also possible by a slight modification of the apparatus. The test tube ( $4'' \times \frac{1}{2}''$ ) is drawn out to a constriction (Fig. 26*b*) an inch below the side tube, and a glass bead is placed so that it loosely fills the constriction and allows the vapour to pass through easily. The tube is

then filled with small glass beads to a height of about half an inch below the side-tube and the bulb of the thermometer remains just above the layer of glass beads. Distillation can be carried out by heating with a micro-burner on an asbestos centred wire-gauze or more simply by heating on an asbestos sheet with a tiny hole at the centre. The distillation tube is wrapped in thin asbestos paper up to the neck.

### **Extraction of small amounts of substances by solvents.**

The substance to be extracted is placed in a small tube ( $3'' \times \frac{1}{2}''$ ) and a few c.c. of the solvent (ether or other solvents) are added. The tube is then closed with a cork and the contents thoroughly shaken. The liquid is allowed to settle or if the original be an aqueous solution, allowed to separate into layers. The extract containing the substance is transferred to another similar tube by a capillary siphon arrangement as described previously. If the liquid is in two layers as when dealing with aqueous solutions or suspensions, discretion is to be used in siphoning the extract which will be the top layer if ether is the solvent or the bottom layer if heavier liquids like chloroform etc., are used as solvents. The extract should be dried and the solvent removed by evaporation.

The extract can also be removed by suction through a pipette made from a tube of 3-4 mm. bore drawn out to a long capillary of 1 mm. at one end. The capillary end should dip into the extract and gentle suction applied through a rubber tube attached to the other end. (Fig. 27).

Another simpler method of carrying this out is to use a small test-tube with a side-tube fused at about the middle of it. The tube contains the solution to be extracted up to the height of the side-tube. The side-tube is closed with a short bit of rubber tubing and a screw clamp (Fig. 28). Ether is then added, the tube closed

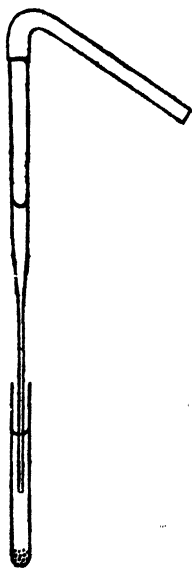


Fig. 27. Use of suction pipette.

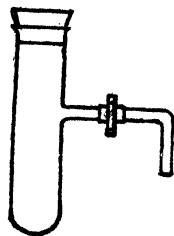


Fig. 28. Apparatus for extracting small quantities.

with a cork or the thumb and the mixture shaken. When the ether layer has separated the screw clamp is opened and the ether extract siphons out of the side-tube and is caught in another tube. The process can be repeated any number of times. The extract after drying is transferred to a small glass dish 1 inch in diameter, which is placed in a small beaker immersed in hot water.

**Heating under reflux.** When small quantities of esters have to be saponified, the process can be carried out in a test-tube

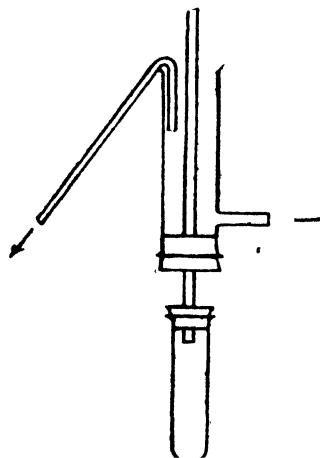


Fig. 29. Heating under reflux.

(6"  $\times$   $\frac{5}{8}$ " or 6"  $\times$  1"). The test-tube is fitted with a one-holed cork carrying a long glass tube 6 mm. in diameter. A small water condenser can be improvised by fixing on the tube the neck of a broken distilling flask. The water enters through the side tube and by adjusting the rate of flow, water can be caused to flow out through the outflow regularly (Fig. 29).

**Expt. (16) Lassaigntest for nitrogen.** A capillary of about 1 mm. diameter and 3" long is taken and sealed at one end. A small crystal of urea or benzamide is mixed with a tiny bit of sodium ( $\frac{1}{2}$  to 1 mm.) by

means of a spatula and this mixture is introduced into the capillary by means of a wire. The tube is heated from the top to the bottom by waving over a flame and when the reaction is over, it is crushed with a little water and ferrous sulphate in a micro-test-tube, heated and centrifuged. The clear solution is siphoned off by capillary into another test tube and acidified with HCl. Flakes of prussian blue appear on standing.

**Test for sulphur.** Soda-chlorate mixture is first made by mixing 6 parts of anhydrous sodium carbonate and 1 of potassium chlorate. A fragment of moist thiourea is mixed on a microscope slide with 4 to 10 times the weight of the above mixture and heated over a spirit lamp flame holding the slide slightly above the flame till the reaction is finished. The mass is dissolved in water, transferred to a micro-test-tube and a few drops of dilute hydrochloric

acid and barium chloride are added. A white precipitate of barium sulphate is formed.

**Halogens : Beilstein test.** A little powdered copper oxide (wire form) is placed in the loop of a platinum wire and heated for a few seconds. This process is to enable the copper oxide to stick to the wire. The substance under test is dusted or sprayed on the loop and introduced into the perfectly nonluminuous flame of a Bunsen burner first in the inner and then in the outer flame. The characteristic blue or green colour appears.

The reaction is so sensitive as to enable the detection of the halogen contained in a one per cent solution of chloroform in alcohol. A blank test should first be made, using alcohol alone.

**Preparations. Expt. (17) Nitrobenzene.** In a micro test-tube of 1-2 c.c. capacity are placed four drops of concentrated sulphuric acid and 3 of concentrated nitric acid and three drops of dry benzene are then added. The mixture is stirred by a thin glass rod without warming and suspended in a hot water bath at 60° for half an hour. Three drops of water are now added, the mixture transferred to a centrifuge cone and centrifuged whereby the nitrobenzene is collected at the bottom as a single drop. It is washed using the capillary siphon till the wash-liquid is free from acids, and nitrobenzene is then dried by immersion of the cone in a boiling water bath. The b.p. of the sample is then determined by the micro-method.

**Expt. (18) Reduction of nitrobenzene to aniline.** In a 3" test-tube, two drops of nitrobenzene and 0.1 g. of tin foil, weighed on a balance and rolled into a small ball, are put in. Concentrated hydrochloric acid (6 drops) is added, the mixture is cooled during addition and the tube set aside for about 15 minutes. If the odour of nitrobenzene has not disappeared, the mixture is warmed on the water bath and more tin and hydrochloric acid are added. On cooling, the liquid becomes a pasty solid. Strong potassium hydroxide solution (50%) is added drop by drop and the aniline extracted with ether. Into the test-tube 1 c.c. of ether is poured and the contents stirred up with a pointed glass rod and centrifuged. The ether extract is siphoned off into a micro-beaker by capillary siphon. The extraction is repeated once or twice and the combined extracts evaporated on water bath.

**Test.** A little of the aqueous solution of aniline is treated with

a little bromine water. A white precipitate of tribromoaniline is formed.

**Expt. (19) Saponification of ester.** 1 g. of methyl salicylate is taken in a boiling tube, 10 c.c. of bench alkali (2N. NaOH) are added and refluxed as described (page 38) for an hour or two by heating on a tiny flame over a wire gauze. The solution is cooled, nearly neutralised with dilute sulphuric acid and the liquid distilled in a distillation apparatus as in Fig. 26 by heating gently till half of the liquid has distilled over. The distillate contains an aqueous solution of methyl alcohol which can be tested for even in dilute solution as described below.

**Test for methyl alcohol.** Two to three drops of the above distillate are placed in a small crucible of 2-3 c.c. capacity and a piece of copper gauze, 2 cm.  $\times$  2 cm., made into a small roll is heated to a bright red heat in a Bunsen flame and quickly dipped into the crucible. A microscope slide, on the under surface of which a drop of an aqueous solution of dimethyl dihydroresorcin (dimedone) is suspended, is quickly placed over the crucible. The formaldehyde formed interacts and forms formal-dimedone which crystallises in fine needles and can be recognised under the microscope.

## TESTS FOR PURITY :

### Determination of melting and boiling points

The purity of an organic compound is always determined by finding its melting point if solid, or its boiling point, if liquid.

**Melting points of solids.** A solid substance when pure melts sharply at a definite temperature. When associated with impurities it will usually soften and look like thawing in, long before the melting point is reached, becoming finally fluid only on continued heating ; there is generally a wide difference in temperature between the softening point and the point at which the substance completely melts. This behaviour is an indication that the substance is impure and requires recrystallisation.

**Requisites for determining melting point.** The most important requisite is a good thermometer with a small bulb and a suitable range. For substances melting below  $100^{\circ}$  the range of the thermometer may be  $0-110^{\circ}$ . For higher temperatures a range up to  $360^{\circ}$  may be used. In all cases the thermometer

should be standardised using pure substances whose melting points have been corrected for stem exposure.

The simplest type of apparatus consists of a 100 c.c. beaker supported on a tripod over a wire gauze and containing concentrated sulphuric acid up to a convenient level (Fig. 30*a*). A stirrer made from glass rod and with a long handle is used for mechanical agitation. The thermometer is inserted into a one-holed cork and clamped in position with the bulb well immersed in the acid about 1 cm. above the bottom of the beaker and in the centre of the beaker. The heating may be carried out by means of a micro-burner. This apparatus, though simple, has the drawback that the sulphuric acid is always exposed to atmospheric moisture and cannot be regarded as a permanent set up. The acid should be kept every time after use in a stoppered bottle as it will absorb moisture.

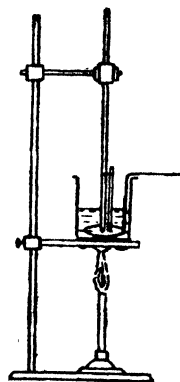


Fig. 30 (*a*) Simple apparatus for melting point determination.

The best apparatus to set up consists of a round bottom flask of about 200 c.c. capacity with a test-tube hanging freely in the flask and resting on the flanged lip. Both the inner tube and the outer flask are filled to the same height with the bath liquid. The test-tube is fitted with a one-holed cork, split so that the whole of the thermometer scale may be visible. No stirring is necessary as the liquid in the inner tube is heated uniformly by the liquid in the outer bath through convection currents (Fig. 30*b*).

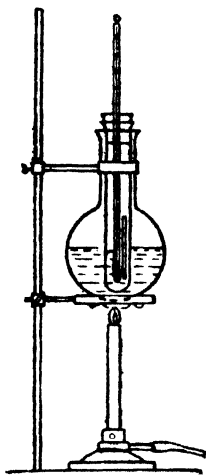


Fig. 30 (*b*) Apparatus for melting point determination.

It is convenient to set up two such flasks, one for higher and the other for lower temperatures. For temperatures between 0 to 220° colourless concentrated sulphuric acid, sp. gr. 1.848, is used. If the acid in the inner tube gets coloured through contact with organic matter, it can be easily decolourised by adding a crystal of potassium nitrate and heating.

For temperatures between  $220^{\circ}$ — $300^{\circ}$ , the bath liquid is prepared by heating 70 parts of concentrated sulphuric acid with 30 of potassium sulphate in a porcelain basin until the boiling stops. The mixture has the consistency of glycerine and does not fume badly. It is less corrosive and less easily rendered brown by organic matter.

Melting point determinations are carried out in capillaries which have to be specially made.

**Determination of melting point.** The substance whose melting point is to be determined is powdered, and pressed on a piece of porous tile by means of a spatula to remove any traces of moisture and then heaped to a little mound at the centre of the bit of tile. One end of the capillary is closed by drawing it across the flame and the open end is pressed on the little mound so that a column is held firmly in the tube. On inverting the capillary and gently tapping, the loosened powder falls down. The substance should occupy a column of 1 to 2 mm. in the capillary. The melting-point tube is then attached, by moistening it with the liquid of the bath, to the lower end of a calibrated thermometer so that the substance is at the level of the middle of the thermometer bulb. The bath is heated steadily by a small flame with stirring. Substances which melt without decomposition may be heated at the rate of about  $2^{\circ}$  per minute, while substances which tend to decompose in the neighbourhood of their melting points should be heated more rapidly at about  $5^{\circ}$  per minute. The temperature recorded just before the moment of liquefaction will generally be nearer the true melting point. In practice the tendency is to record the temperature at which the first drop of clear liquid is formed, as this is much easier to observe. The determination of the m.p. is to be repeated twice or thrice and the average taken.

**Expt. (20)** Determine the melting points of the following substances :

(a) using water as bath liquid : (1) o-Nitrophenol ; (2) Urethane ; (3) m-Dinitrobenzene ; (4) Vanillin ; (5)  $\beta$ -Naphthyl methyl ether ; (6) p-Nitro-chlorobenzene.

(b) using sulphuric acid as bath liquid : (1) Benzoic acid ; (2) Benzoin ; (3) Urea ; (4) Salicylic acid ; (5) Benzanilide ; (6) Phthalimide ; (7) Oxanilide.

**Mason's apparatus.** This is intended for the determination of melting points of substances between  $200^{\circ}$ — $400^{\circ}$ , which cannot

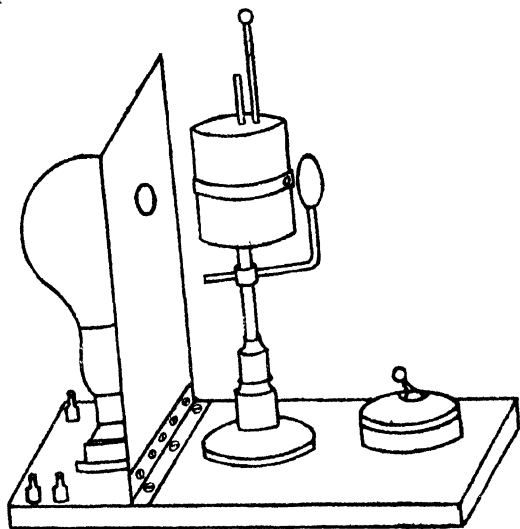


Fig. 31. Mason's apparatus.

be so conveniently determined using a liquid bath owing to the tendency of sulphuric acid to fume strongly at high temperatures. The apparatus (Fig. 31) is electrically heated and consists essentially of a small metal cylinder either of copper or brass with two vertical holes one for a thermometer and the other for the melting-point tube; there is also a central hole at right-angles to the above for observation of the substance in the melting-point tube. The heating element is nickel-chrome wire covered with asbestos and wound round the cylinder. Illumination is provided by an incandescent lamp behind and a small magnifier is placed in front to observe the substance. For use on 220 volts an additional resistance is provided, by adjusting which, the rate of heating can be controlled. Without this resistance it can be used only on a 100 volt circuit. The determination of melting points can be made with the same precautions as described previously.

**Mixed melting points.** Sometimes when, as a result of analysis, a substance is suspected to be identical with a known organic compound it may further be confirmed by taking the



mixed melting point. The test depends on the principle that impurities generally lower the melting point of a compound. To determine whether two substances having the same melting point are one and the same, the two are mixed in about equal quantities and the melting point of the mixture taken. If the melting point is not lowered, then the two substances are recognised as identical.

**Boiling points.** The type of apparatus to be used depends upon the quantity of liquid available for carrying out a determination. When a few c.c. of the liquid are available the **distillation** method may be employed observing certain precautions. Five to six c.c. of the dry liquid are placed in a distilling flask of about 10 c.c. capacity fitted with a one-holed cork, carrying a thin stemmed thermometer. The neck of the flask should be as short as possible. Light capillary tubes 1 to 1.5 mm. diameter and of a length sufficient to rest against the sides of the flask below the surface of the liquid are dropped into the flask to prevent bumping and promote steady boiling. One or two pieces of porous porcelain

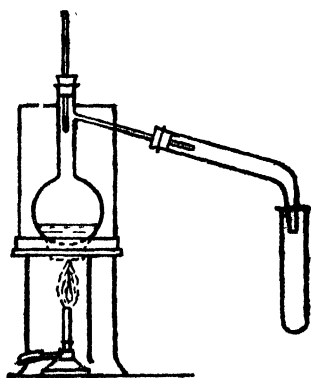


Fig. 32 (a) Apparatus for determination of boiling points of liquids.

may also be used instead of the capillaries. The flask is enclosed in a hood made from thin asbestos sheet. It is rested on a square piece of asbestos board with a hole of 2 cm. diameter at the centre. The flask should sit tight, so that close contact is secured on all portions of the opening. This is necessary to guard against superheating by the escape of hot gases. If necessary, a washer from asbestos paper may also be inserted. An air-condenser (length 10 inches, bore  $\frac{1}{2}$  inch) is attached to the

side-tube and the flask is heated by a micro-burner so as to distil slowly at the rate of half a c.c. per minute, the distillate being collected in a dry test tube (Fig. 32a). The thermometer reading when the first two drops have collected should be discarded. The average of several readings recorded at half c.c. intervals should be taken. Distillation should be stopped when less than 1 c.c. remains in the flask. When inflammable liquids are distilled a filter flask or tube should be used as receiver.

**Boiling points of small quantities.** When only a few drops of a liquid are available, three drops of the liquid are introduced by means of a capillary into a narrow glass tube 3 mm. diameter and 6 to 7 cm. length (a micro-test-tube) closed at one end. This tube is attached to a thermometer by a rubber ring with the liquid opposite the bulb. Into the liquid is placed the open end of a sealed melting-point capillary. The thermometer with the tube is placed in the melting point apparatus (Fig. 32*b*) which is heated slowly. At first air bubbles are expelled from the capillary due to expansion by heat. Finally a point is reached at which there is a regular stream of bubbles emitted from the tube. This temperature is taken as the boiling point. At least three observations are to be made and the mean taken as the true boiling point.

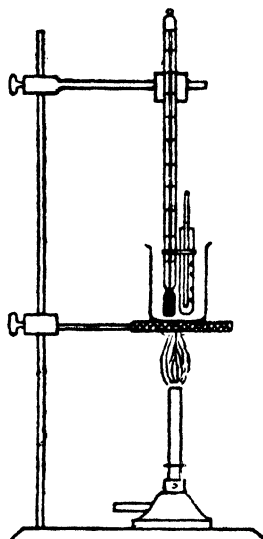


Fig. 32 (*b*)  
Semi-Micro-determination of  
boiling point.

**Micro-method.** An accurate boiling point determination can be made with a minute drop of liquid (note preparation of nitrobenzene in expt. 17). A capillary, 1 mm., diameter, is drawn out very fine at one of its ends using a micro-flame. The drop of liquid contained in a microscope slide or the micro-test-tube is just touched with the drawn out capillary. A column (*L*) of liquid is drawn in. When the volume is approximately 1 c. mm., i.e., 1 mm., in the capillary, the tube is waved over a flame, so that the liquid expands and encloses a minute air bubble (*A*). The fine point is touched by the edge of the flame which seals up the air. The sealed capillary is stuck up on a microscope slide with a drop of liquid. The microscope slide has a thermometer fastened on to it. The system is immersed in a heating bath containing glycerine or paraffin oil and provided with a stirrer (Fig. 33). On heating up, the air bubble expands slowly till the boiling point is reached and then suddenly increases in volume driving the drop of liquid

to the level of the surface (S) of the bath. This temperature is taken as the boiling point of the substance.

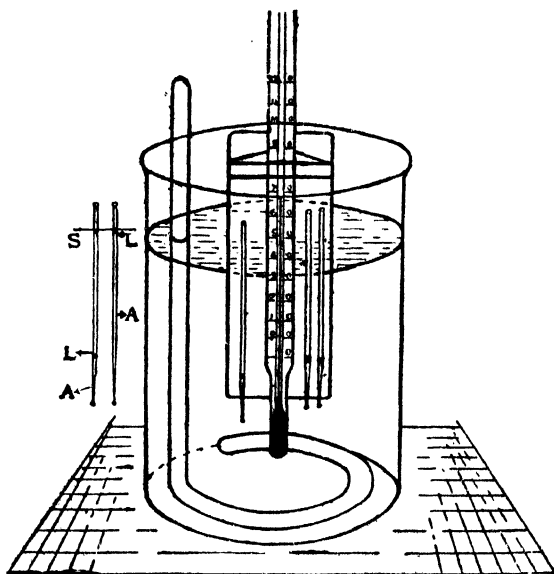


Fig. 33. Micro-determination of boiling points.

**Expt. (21)** Determine the boiling points of the following liquids both by ordinary and micro-methods :—

- |                          |                   |
|--------------------------|-------------------|
| (1) Carbon tetrachloride | (4) Nitrobenzene  |
| (2) Chlorobenzene        | (5) Toluene       |
| (3) Benzene              | (6) Ethylbenzoate |

**Corrections to be applied to thermometer readings during melting and boiling point determinations.** The thermometer readings as ordinarily taken during melting or boiling point determinations, are subject to two sources of error, namely, (a) errors due to a faulty graduation and (b) errors caused by exposure of a portion of the mercury column to atmospheric cooling. In the first case a long scale thermometer ( $0^{\circ}$ — $360^{\circ}$ ) as is ordinarily used may be calibrated by finding the melting points or boiling points of a number of pure substances whose corrected melting or boiling points are known. The observed melting or boiling points are plotted against the correct ones. From the resulting

curve the true melting point or boiling point corresponding to any observed value can be found out.

**Stem correction.** In all melting or boiling point determinations the mercury column is not entirely at the temperature of the mercury in the bulb. The portion of the mercury column above the surface of the liquid in a melting-point determination or above the cork in a distillation flask is cooled by the surrounding atmosphere and the registered temperature is somewhat low. In the case of temperatures below  $100^{\circ}$ , the cooling effect does not cause any great error but for higher temperatures the reading may be  $3^{\circ}$  to  $8^{\circ}$  below the correct temperature. To minimise this error a correction calculated from the formula given below may be applied :

$$T_1 \text{ (corrected)} = T_0 + \cdot 000156 (T_0 - T_a)l.$$

where  $T_0$  = observed temperature.

$T_a$  = average temperature of the middle point of mercury column taken by another thermometer hung by the side.

$l$  = length of mercury column in degrees above the surface of liquid in melting point determinations or above the cork in boiling point determinations.

### Calibration of thermometer

The thermometer should always be calibrated by observing the melting points of several pure compounds such as the following :

M.P. (corr.)	M.P. (corr.)
0° ... Ice	187° ... Hippuric acid
53 ... p-Dichlorobenzene	200 ... Isatin
90 ... m-Dinitrobenzene	216 ... Anthracene
114 ... Acetanilide	238 ... Carbanilide
121 ... Benzoic acid	257 ... Oxanilide
132 ... Urea	286 ... Anthraquinone
157 ... Salicylic acid	317 ... N, N-Diacetyl benzidine.

If care is taken to use the same apparatus and thermometer in all melting-point determinations, it is convenient and time-saving to prepare a calibration curve such as that shown in Fig. 34. The observed melting point of the standard compound is plotted against the corrected value, and a curve, OA, is drawn through these

points. In subsequent determinations the observed value, B, is projected horizontally to the curve and then vertically down to give the corrected value, C.

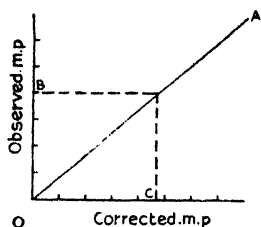


Fig. 34

It should be noted that such a calibration curve includes corrections for inaccuracies in the thermometer and stem correction.

It is important to record the melting-point range of an unknown compound since this is a valuable index of purity.

A large majority of pure organic compounds melt within a range of  $0.5^{\circ}$  or melt with decomposition over a narrow range of temperature (about  $1^{\circ}$ ). If the melting-point range or decomposition range is wide, the compound should be recrystallized from a suitable solvent and the melting or decomposition point again determined.

## CHAPTER III

### REACTIONS OF COMMONER ORGANIC COMPOUNDS CONTAINING CARBON AND HYDROGEN WITH OR WITHOUT OXYGEN

The majority of simple organic compounds are members of homologous series possessing definite chemical properties by virtue of their possessing such groups as carboxyl, hydroxyl, carbonyl, nitro, amino etc., while the more complex organic substances contain two or more of these groups. Reactions carried out with the object of detecting these are usually called group or classification reactions. They should be carried out with known organic compounds of each class before commencing systematic analysis, particular attention being paid to the conditions under which each reaction takes place. Preliminary experience gained in this way is of immense help in the rapid analyses of organic substances.

**Reactions of hydrocarbons.** Hydrocarbons are the parent substances from which all other substances may be derived and they are generally the least reactive. Hydrocarbons can be grouped into aliphatic and aromatic (cyclic), saturated and unsaturated.

#### Aliphatic hydrocarbons

(a) **Saturated.** Use ligroin (b.p. 70-120°) or n-Hexane (b.p. 71-75°) or n-Heptane (b.p. 99°). The latter occur in ligroin.

(1) Introduce a few drops of the liquid at the end of a flattened nickel wire into the non-luminous flame of the Bunsen burner. Note that they are all combustible, the flames being luminous but not quite sooty. A carbon residue is left in the case of the higher members.

(2) Warm a few drops with 2 c.c. of concentrated sulphuric acid: no change is seen. The liquid remains immiscible. Saturated hydrocarbons may be distinguished from unsaturated and aromatic hydrocarbons by their insolubility in concentrated sulphuric acid.

(3) Warm a drop or two with 2 c.c. of alkaline permanganate: no decolorisation takes place.

(4) Repeat experiment (2) using 1 c.c. of fuming nitric acid: no signs of oxidation are visible.

(5) Mix in a small test tube a few drops of the hydrocarbon with a drop of pure bromine and a small quantity of iron filings and heat : hydrogen bromide is evolved showing that substitution has taken place.

(b) **Unsaturated.** Use Amylene  $[(CH_3)_2 C=CH \cdot CH_3]$  (b.p.  $35-36^\circ$ ).

**Tests for unsaturation.** (1) *Bromine test* : Dissolve or suspend about 0.1 g. of the substance, finely powdered if solid, in 2 c.c. of dry carbon tetrachloride. Add three drops of a solution of bromine in carbon tetrachloride and shake if necessary. Note the following effects :

Instantaneous decolorisation *without evolution of hydrogen bromide* shows a double or *treble* bond. In some cases decolorisation may not take place in the cold. Heating, sometimes even to boiling, may start the reaction, in which case bromine should be added drop by drop till the colour is permanent. No hydrogen bromide should be evolved if bromine is added to the molecule.

(2) Heat in a dry test tube two or three drops, if liquid, or 0.1 g., if solid, with 2 c.c. of concentrated sulphuric acid. If there is a sign of solubility, an unsaturated hydrocarbon may be inferred.

(3) To 0.1 g. of substance in 5 c.c. of 5%  $Na_2CO_3$  solution, add drop by drop 1% potassium permanganate. Unsaturated compounds decolorise permanganate even in the cold with precipitation of brown oxides of manganese, while saturated ones do not.

### Aromatic hydrocarbons

The typical reactions of aromatic hydrocarbons distinguishing them from aliphatic compounds are :—

1. Direct sulphonation.
2. Direct nitration.
3. Oxidation of side chains.
4. Reactivity with chloroform in the presence of anhydrous aluminium chloride.

### Benzene

A colourless liquid lighter than water, immiscible and burning with a highly sooty flame, b.p.  $80.3^\circ$ .

(1) To 2 c.c. of fuming sulphuric acid contained in a small test-tube introduce 0.5 c.c. of benzene from a capillary pipette.

Shake for two or three minutes without heating. The oily layer will disappear. Pour the mixture into 10 c.c. of water contained in a test tube ( $6'' \times 1''$ ) cooled under water, stirring all the while with a glass rod and add 2 to 3 g. of solid sodium chloride. Decant from undissolved sodium chloride and cool in ice. Sodium benzene sulphonate separates after a time in lustrous plates. Filter, wash with 2 c.c. of saturated sodium chloride solution and crystallise from alcohol.

(2) To 1 c.c. of a mixture of concentrated sulphuric acid and nitric acid (2 : 1) add ten drops of the hydrocarbon gradually from a pipette. Immerse the tube in cold water so that the temperature does not rise above  $50-60^{\circ}$ . On diluting with water after a minute, nitrobenzene separates as a heavy yellow oil with a peculiar but agreeable odour.

Tests (1) and (2) are characteristic of aromatic hydrocarbons.

(3) Heat five drops of benzene with 5 c.c. of a 1 per cent solution of alkaline permanganate in a test tube ( $6'' \times 1''$ ) fitted with a cork and a long tube to serve as condenser. No decolorisation takes place.

(4) Dissolve two drops of the hydrocarbon in 2 c.c. of chloroform. Heat in a small dry test-tube a small lump of fresh anhydrous aluminium chloride over a tiny flame until it slowly sublimes leaving a thin coating over the sides of the tube. Drop 0.5 c.c. of the solution, stopper the tube and roll it over till the sublimate gets wetted completely. Observe the colour after a few seconds and again after five minutes.

An orange yellow colour is developed and remains unchanged for a long time.

Most aromatic hydrocarbons give colorations when thus treated and the colours are very intense ; the reaction is therefore of help as a preliminary or a confirmatory test.

(5) *meta*-Dinitrobenzene. Add four drops of benzene to a mixture of 1 c.c. of fuming nitric acid and 1 c.c. of concentrated sulphuric acid contained in a test-tube. Heat for a few minutes on a boiling water bath and pour into water. Filter and recrystallise from alcohol. Colourless needles are obtained. (m.p.  $90^{\circ}$ ).

## Toluene

Colourless liquid lighter than water, b.p.  $110^{\circ}$ .

(1) Repeat experiments (1) and (2) as under benzene. The reactions are similar.



(2) *Oxidation of side chain.* Take 2 c.c. of toluene in a 100 c.c. round-bottom flask, add 2 c.c. of 2N alkali and boil under reflux with continual addition of 3% permanganate solution till the colour persists (about half an hour). Filter off the precipitated manganese dioxide and pass sulphur dioxide through the filtrate. Benzoic acid is precipitated on cooling. Filter, recrystallise from water and find its m.p. ( $121^{\circ}$ ).

(3) *2 : 4, Dinitro-toluene.* To 1.5 c.c. of fuming nitric acid add an equal volume of fuming sulphuric acid (10%) and while the mixture is still hot, drop in four to five drops of the hydrocarbon, shaking during the addition. After two minutes pour into ice water and recrystallise the precipitated nitro compound from 50% alcohol. (m.p.  $70^{\circ}$ ).

### Naphthalene

Characteristic odour, insoluble in water, readily soluble in alcohol, ether and other solvents, m.p.  $80^{\circ}$ .

(1) Dissolve 0.1 g. of finely powdered naphthalene in 2 c.c. of dry carbon tetrachloride. Add a solution of bromine in the same solvent drop by drop and warm. HBr is evolved in plenty which shows bromine substitution.

(2) Test with anhydrous aluminium chloride in the manner prescribed on p. 51 ; a greenish blue colour is produced.

(3) Oxidation (vide experiment 2, under Toluene) gives phthalic acid in small quantities. (m.p.  $195^{\circ}$ ).

(4) Make a saturated solution of naphthalene in 1 c.c. of benzene or alcohol and a similar solution of picric acid; mix the two. A fine golden yellow precipitate of the picrate separates. Filter dry and determine m.p. ( $149^{\circ}$ ).

(5) Add 0.2 g. of solid naphthalene to 1.5 c.c. of concentrated nitric acid. Warm gently on water bath for 2 minutes, pour into water and recrystallise the  $\alpha$ -nitronaphthalene from 5 c.c. of alcohol. Filter and determine the m.p. ( $61^{\circ}$ ).

(6) Add 3 g. of chromic anhydride slowly to a warm solution of 1 g. of naphthalene in 8 c.c. glacial acetic acid. Boil gently for 3 minutes, cool, dilute with water (40 c.c.), filter and wash the precipitated solid. Distil the product in steam, collect the yellow crystals of  $\alpha$ -naphthaquinone, note their pungent odour and determine the m.p. ( $125^{\circ}$ ).

(7) Weigh into a small test-tube ( $4'' \times \frac{1}{2}''$ ) 0.1 g. of the hydrocarbon and 0.15 g. of m-dinitrobenzene and melt the mixture rapidly by immersion in a boiling water-bath. Dissolve the melt in three drops of benzene and add a drop of ligroin. Transfer directly to a piece of porous plate the precipitated addition compound and determine its m.p. ( $51^\circ$ ).

### Anthracene

Usually yellow but white when pure with a violet fluorescence; soluble in alcohol, m.p.  $216.5^\circ$ .

(1) Picrate : Prepared from benzene solution. Unstable ; (m.p.  $138^\circ$ ).

(2) To 0.2 g. of the hydrocarbon contained in a boiling tube ( $6'' \times 1''$ ) fitted with a one-holed cork carrying a long tube, add a solution of 1.5 g. of chromic acid in 4 c.c. of glacial acetic acid. Maintain at gentle boiling for 15 minutes. Pour into cold water. Filter and recrystallise the anthraquinone formed from glacial acetic acid or absolute alcohol, or purify by sublimation. Pale yellow needles are obtained ; (m.p.  $279-280^\circ$ ).

(3) Dissolve 0.1 g. of anthracene in 2 c.c. of dry  $\text{CCl}_4$ . Add a solution of bromine in carbon tetrachloride drop by drop and warm. The dibromo-derivative is formed. Filter, dry and find its m.p. ( $221^\circ$ ).

### Alcohols

The typical reactions of the alcohols are the reactions of the hydroxyl group, viz., with (a) Metallic sodium, (b) Phosphorus pentachloride and (c) Acid chlorides and anhydrides.

#### Methyl alcohol.

A colourless liquid, miscible with water, b.p.  $66^\circ$ .

(1) *Oxidation to formaldehyde.* Roll a piece of copper gauze, two centimetres square, round a copper wire eight inches in length at one of its ends and fix a small cork at the other end to serve as insulating handle. Oxidise the gauze by heating in the Bunsen flame and plunge it while hot into a test-tube containing five drops of methyl alcohol dissolved in 3 c.c. of water. Withdraw the gauze when cold and repeat the process three times. Note the formation of a pungent smelling vapour. Cool the liquid, add two drops of an aqueous solution of resorcinol (0.5%) and pour the liquid into 5 c.c. of concentrated sulphuric acid contained in ano-

ther test-tube carefully so as not to mix the liquids. A dull violet ring is formed at the junction of the two liquids. A white precipitate changing to red-violet forms in the aqueous solution above this ring.

(2) To 1 c.c. of methyl alcohol add 1 g. of powdered sodium chloride and 2 c.c. of concentrated sulphuric acid. Warm gently and set fire to the vapour. Methyl chloride is formed which burns with a green flame.

(3) *Oxidation to formic acid.* Digest in the cold 2 c.c. methyl alcohol under reflux with 5 c.c. of a saturated solution of sodium dichromate and 2 c.c. of sulphuric acid (1:1) till oxidation is complete. Allow the mixture to stand for five minutes and then dilute it with an equal volume of water. Distil till about 1 c.c. of liquid collects and test the distillate for formic acid by adding (*a*) dilute mercuric chloride solution and warming, when white mercurous chloride is precipitated and (*b*) silver nitrate solution and warming, when a silver mirror or a black precipitate of silver is formed.

(4) *Oil of wintergreen test.* Add 2 to 3 drops of concentrated sulphuric acid to 3 drops of methyl alcohol contained in a test-tube, and then a pinch of salicylic acid. Place the test-tube for a few minutes in a beaker of boiling water and then pour the contents into a test-tube containing 5 c.c. of dilute sodium carbonate. Methyl salicylate is formed and is recognized by its pleasant-smell.

(5) *3:5-dinitrobenzoate.* In a small dry test-tube heat together 0.3 g. of 3:5-dinitrobenzoic acid and 0.4 g. of phosphorus pentachloride over a tiny flame. Continually rotate the tube and allow the mixture to boil gently for a minute. Pour the liquid into a dry watch-glass. Allow the melt to solidify and remove the liquid phosphorus oxychloride by a filter paper. Take the dry solid in a dry test-tube, add eight drops of methyl alcohol, stopper the tube and shake. Recrystallise the solid ester from dilute alcohol (3 volumes of alcohol to 1 of water). Filter hot and cool the filtrate. The ester crystallises in shining leaflets. (m.p. 107-108°).

### Ethyl alcohol

Colourless liquid, b.p. 78.4°.

(1) *Reaction with sodium.* In a test-tube with a side tube place 3 c.c. of absolute alcohol and attach a delivery tube to the

side-tube by a rubber-tubing. Add a piece of clean sodium (2 mm. square) ; quickly close the mouth of the tube with a cork collecting the gas over water. Test the gas for hydrogen. Add further bits of sodium till the reaction slackens. Evaporate the solution on a water-bath to dryness. Sodium ethoxide is obtained as a solid.

N.B. This test with sodium is given by almost all the alcohols and phenols and the only condition is that the alcohol should be dry. Solid alcohols are dissolved in dry benzene or carbon tetrachloride and warmed with sodium by heating on water-bath, but the reaction is somewhat slow.

(2) *Formation of Ethyl Chloride.* Place a few granules of phosphorus pentachloride in a test-tube with side-tube ( $6'' \times \frac{3}{4}''$ ). Fit it with a cork carrying a small dropping funnel. Attach a small empty wash-bottle ( $4'' \times 1''$ ) to the side-tube and finally a delivery tube. Drop ethyl alcohol and collect the gas over saturated brine in a test-tube. Ethyl chloride along with hydrogen chloride is liberated and the latter is absorbed by the brine. On setting fire to the gas, it burns with a green-edged flame.

(3) *Oxidation to Acetaldehyde.* To 1 c.c. of dilute sodium dichromate solution (N/2) add a drop or two of concentrated sulphuric acid and then six drops of alcohol. Heat gently and note the change in colour of the solution to green and the characteristic smell of acetaldehyde.

(4) Repeat experiment (3) in a test-tube with side-tube and collect the acetaldehyde vapour in 2 c.c. cold water. Add 2 drops of Schiff's reagent and note the characteristic pink colour appearing slowly.

(5) *Iodoform test.* To three drops of alcohol in 3 c.c. of water contained in a test-tube add five drops of strong solution of iodine in potassium iodide and then add drop by drop a 10% solution of sodium hydroxide till a faint yellow colour persists after the solution is shaken. Immerse the test-tube in a beaker of hot water at  $50-60^{\circ}$ . Iodoform with its characteristic smell settles down, in the form of minute yellow crystals.

N.B. A number of substances give this test : Acetone, Isopropyl alcohol and Allyl alcohol.

(6) *Ethyl Acetate test.* To 0.5 g. of fused sodium acetate in a test-tube add ten drops of alcohol and then 2 c.c. of concentrated sulphuric acid. Gently warm and pour the mixture into dilute

sodium carbonate solution. A fruity odour of ethyl acetate is perceived.

(7) To 1 c.c. of alcohol in a test-tube add an equal volume of acetyl chloride drop by drop keeping the test-tube immersed in cold water. Hydrogen chloride is liberated. Pour the contents of the tube into 5 c.c. of cold water carefully. Ethyl acetate is formed.

(8) Repeat the above experiment using acetic anhydride. Place a glass rod with a trace of concentrated sulphuric acid in the mixture to start the reaction. Pour into cold water as before and note the formation of ethyl acetate.

(9) *para*-Nitrobenzoate. Dissolve about 0.2 c.c. (four drops) of the alcohol in 1 c.c. of water, add 0.5 g. of p-nitrobenzoyl chloride and then 2 to 3 c.c. of ether. Shake vigorously for a few minutes. Add sodium hydroxide solution till the solution is alkaline to phenolphthalein. Separate the ether extract by a suction pipette and evaporate off the ether. The p-nitrobenzoate (m.p. 57°) obtained in well defined crystals is almost pure and can be further purified by crystallisation from light petroleum. With the pure alcohol the precipitation takes place at once.

### Allyl alcohol

Colourless liquid with an unpleasant pungent odour, miscible with water, b.p. 97°.

(1) To two drops of allyl alcohol add 2 c.c. of acidified potassium dichromate solution. On warming, acrolein is evolved with an irritating odour.

(2) To a few drops of allyl alcohol add bromine water. Instant decolorisation takes place with formation of dibromopropyl alcohol  $\text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{CH}_2\text{OH}$  having a pleasant smell.

(3) Reactions with sodium and phosphorus pentachloride, and the iodoform reaction are carried out as with ethyl alcohol. All the tests are answered so that allyl alcohol behaves both as a primary alcohol and as an unsaturated compound.

### Glycerol

Colourless, syrupy liquid boiling with slight decomposition at 290°.

(1) *Colour reaction* : Applicable even to dilute aqueous solutions.

To one drop of glycerine in 2 c.c. of cold water add five drops of a 1% aqueous solution of pyrogallol and 2 c.c. of concentrated sulphuric acid and shake. Boil the mixture for a few seconds, cool at once in tap-water and dilute to about 10 c.c. with absolute alcohol. A characteristic purplish red colour is developed fading after sometime.

(2) *Acrolein test* : Take 1 g. of powdered potassium bisulphate in a test-tube, add about five drops of glycerol and stir with a glass rod so that a paste is formed. Fit the test-tube with a one-holed stopper carrying an L-tube and heat the test-tube gently at first and more strongly afterwards. Pass the vapours into a test-tube containing 2 c.c. of water. Acrolein obtained is recognized by (a) its irritating odour, (b) decolorising bromine water, (c) restoring the pink colour to Schiff's reagent, and (d) reducing ammoniacal silver nitrate.

(3) *Borax test* : To 2 c.c. of 1% borax solution add two drops of phenolphthalein. A red colour is developed. Add now a neutral aqueous solution of glycerine (1 : 1) drop by drop until the colour is destroyed. Heat the solution to boiling and note the reappearance of the colour which is lost once again on cooling.

Glucose and other polyhydric alcohols also give this reaction which is due to the hydroxy compound combining with the boric acid to form a much stronger acid.

(4) To 5 c.c. of a 10 per cent. aqueous solution of glycerol add a solution of ammoniacal silver nitrate and warm. A black deposit of metallic silver is obtained.

(5) *Glyceryl tribenzoate* : In a round bottom flask of capacity 100 c.c. place 4 g. of glycerol and about 30 c.c. of 10% caustic soda. Add 3 c.c. of benzoyl chloride, a little at a time, cork the flask and shake well after each addition. Cool under the tap, see that the liquid is alkaline and when the addition is complete, decompose the excess of the acid chloride by heating on a water bath for about 15 min. On cooling and shaking, the benzoyl derivative solidifies. Filter the precipitate wash with cold water and recrystallise from dilute alcohol, (2:1). Filter the crystals, wash with dilute alcohol, and press on a porous plate. Dry the solid and find its m.p. (71-72°).

(6) *Denige's test*. (a) 0.1 g. of glycerol is mixed with 10 c.c. of freshly prepared bromine water and the mixture heated

on the water bath for 20 minutes and then boiled to expel the bromine.

(b) Two drops of a solution of salicylic acid (1 g. in 30 c.c. of absolute alcohol) is mixed with eight drops of the solution obtained in (a) and two drops of a 4% solution of potassium bromide. 2 c.c. of sulphuric acid (sp. gr. 1.84) are then added, when a raspberry colour is developed in 1 or 2 minutes. Any phenolic compound can replace salicylic acid. Guaiacol gives a blue, and gallic acid a deep violet coloration.

The glycerol is oxidised to dihydroxy acetone in (a) and this forms characteristic coloured condensation products with phenolic compounds.

### **Benzyl alcohol**

Colourless liquid with a faint agreeable odour and sparingly soluble in water, b.p. 206°.

(1) *Formation of Benzyl chloride.* The action of sodium and phosphorus pentachloride on benzyl alcohol are the same as with ethyl alcohol. Benzyl chloride is obtained in the latter case as a colourless liquid with a high boiling point (b.p. 176°).

(2) To 1 c.c. of benzyl alcohol in a test-tube add 2 c.c. of concentrated hydrochloric acid and gently boil the mixture continuously for a few minutes. Cool and note the pungent smell of benzyl chloride.

(3) *Oxidation by nitric acid.* Mix together 1 c.c. of concentrated nitric acid, 4 c.c. of water and three drops of the alcohol in a test-tube. Boil the mixture for about two minutes and note the odour from time to time. The characteristic smell of benzaldehyde is first obtained and disappears as continued oxidation takes place. On cooling the solution, benzoic acid crystallises out. Filter the precipitate and find its m.p. (121°).

(4) *Oxidation by chromic acid.* In a distillation flask of about 25 c.c. capacity take two drops of chromic acid mixture (see Appendix), 10 c.c. of water and five drops of the alcohol. Heat over a micro-burner with constant shaking till the mixture becomes green, keeping the solution below the boiling point. Distil the mixture collecting about 2 c.c. of the distillate in a test-tube containing 1 c.c. of cold water. To the distillate add 3 c.c. of water, 12 drops of alcohol and one drop of phenyl hydrazine and boil for

a minute. Cool, shake well and filter the precipitate. Recrystallise from a little boiling alcohol, filter and dry the crystals and find the melting point of the benzaldehyde-phenylhydrazone ( $156^{\circ}$ ).

(5) *Benzyl Acetate test.* Add acetyl chloride drop by drop to 1 c.c. of the alcohol till no further reaction takes place. Pour the product into cold water containing a little sodium carbonate. Note the characteristic floral odour (jasmine) of the ester formed (Benzyl acetate).

### Aldehydes

The typical reactions of aldehydes may be summarised as follows from the standpoint of qualitative analysis :

1. Regeneration of colour with Schiff's reagent.
2. Reducing action on Tollen's and Fehling's reagents.
3. Formation of bisulphite compound.
4. Condensation reactions with phenyl hydrazine and semicarbazide.

### Formaldehyde

A gas with a characteristic pungent smell and obtainable in 35-40% aqueous solutions known as "formalin."

For reactions use formalin diluted with four times its volume of water unless otherwise specified.

*Colour reactions.* (1) Repeat test on p. 53 for formaldehyde.

(2) Repeat the above experiment using six drops of a saturated alcoholic solution of gallic acid. A pure blue ring appears.

(3) Add a drop of the diluted formalin to 5 c.c. of Schiff's reagent. A bluish-red colour appears in the course of a minute and deepens to purple on standing.

(4) *Schryver's test.* To 10 c.c. of the dilute solution add 2 c.c. of a 1 per cent solution of phenyl hydrazine hydrochloride (freshly made and filtered), 1 c.c. of 5 per cent. potassium ferricyanide and 5 c.c. of concentrated hydrochloric acid. A brilliant magenta colour is developed.

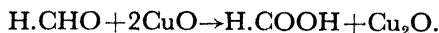
(5) *Reducing action of formaldehyde.* Clean thoroughly a test-tube by boiling a few c.c. of sodium hydroxide solution in it and then washing with distilled water. Place in the test-tube 5 c.c. of Tollen's reagent (ammoniacal silver nitrate) and add 1 c.c.



of the dilute solution of formaldehyde. Immerse the test-tube in a beaker of hot water. A brilliant silver mirror is deposited slowly.

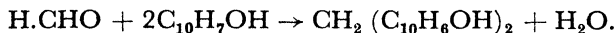


(6) Add 1 c.c. of the dilute solution to 5 c.c. of Fehling's solution and heat to boiling. Red cuprous oxide is precipitated.



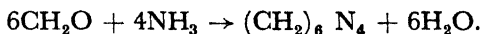
(7) *Polymerisation.* Evaporate on a water-bath 10 c.c. of formalin. A white residue is left behind which sublimes at  $120^\circ$ , and on heating, gives formaldehyde back again, easily recognized by its smell.

(8) (a) *Formation of condensation products.* To three drops of formalin, add 3 c.c. of dilute alcohol (1:2), then about 0.05 g. of  $\beta$ -naphthol and three drops of concentrated hydrochloric acid. Boil gently. Colourless needle-shaped crystals are deposited. Collect the precipitate and recrystallise from dilute alcohol (1:1). Filter and dry the precipitate and determine its melting point. The precipitate is methylene di- $\beta$ -naphthol.



It turns brown at  $180^\circ$  and melts at  $192^\circ$  with decomposition.

(b) *Hexamethylene tetramine.* In a 100 c.c. distilling flask place 15 c.c. of formalin, and add 12 c.c. of ammonia (sp.gr. 0.88) in small quantities with cooling, cork the flask and leave overnight. Next day add another 5 c.c. of ammonia. Shake the solution with a little Norit, filter and evaporate on a water bath under reduced pressure, till a pasty mass is left behind. Boil with absolute alcohol and filter hot. Colourless crystals of hexamine are obtained on cooling. Filter, wash with alcohol and dry. Yield, 4 g. m.p.  $280^\circ$ .



### Acetaldehyde

A colourless liquid, soluble in water in all proportions, b.p.  $20.8^\circ$ .

All the reactions given below can be carried out with an aqueous solution of the aldehyde which is made by either of the following methods:—

(a) In a 50 c.c. round bottom flask, place 5 c.c. of a saturated solution of sodium dichromate and add to it slowly a mixture of 4

c.c. of alcohol and 2 c.c. of concentrated sulphuric acid. After five minutes add 10 c.c. of water, attach a long delivery tube bent

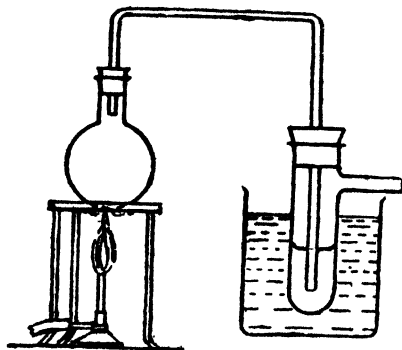


Fig. 35. Apparatus for preparation of small quantities of aldehyde.

twice at right angles and distil using a small flame collecting the distillate (about 10 c.c.) in a test-tube with side-tube surrounded by ice (Fig. 35).

(b) Fit up the apparatus as in the previous experiment, place 10 c.c. of paraldehyde, add 1-2 c.c. of dilute sulphuric acid and heat gently using a micro-burner so that the temperature of the vapour does not rise above  $35^{\circ}$ . Absorb the vapour in 5 c.c. of water contained in the test-tube cooled in ice.

N.B. Addition of too much sulphuric acid causes carbonisation. Benzene sulphonc acid or toluene sulphonc acid (1-2 g.) may be used with advantage.

(1) *Schiff's aldehyde test.* To 5 c.c. of the Schiff's reagent add a drop of the aqueous solution. A pink colour is produced in a few seconds.

(2) *Reducing action on* (a) ammoniacal silver nitrate and (b) Fehling's solution is carried out exactly as with formaldehyde, with the same result.

(3) Add 5 c.c. of a 10 per cent. sodium hydroxide solution to 1 c.c. of the aqueous solution contained in a test-tube and heat slowly to boiling. The solution at first becomes clear yellow in colour, and then dark and finally turbid with separation of brown aldehyde-resin which has a disagreeable odour.

(4) To 5 c.c. of a saturated solution of sodium bisulphite (freshly prepared) contained in a test-tube add 2 c.c.

est aldehyde solution and shake vigorously. A white crystalline precipitate of the bisulphite compound is obtained. Filter the crystals and wash with a few drops of alcohol. Treat a small amount of the crystalline compound with 5-6 c.c. of a 10 per cent sodium carbonate solution in an ordinary test-tube and gently warm. The smell of aldehyde is perceived.

(5) Dissolve 0.2 g. of  $\beta$ -naphthol in 2 c.c. of cold glacial acetic acid to which two drops of concentrated hydrochloric acid have been added. Then add 0.5 c.c. of the aldehyde solutions, shake the mixture thoroughly, gently warm for about five minutes, and then heat slowly to boiling for a couple of minutes. Cool the mixture and shake vigorously adding a drop of alcohol if necessary to start crystallisation. Filter the white crystalline compound, recrystallise from boiling dilute alcohol, dry on a porous plate and find the melting point ( $172-173^\circ$ ). The product is ethylidene di- $\beta$ -naphthol.

### Benzaldehyde

A colourless liquid with the smell of bitter almonds, sparingly soluble in water, b.p.  $179^\circ$ .

(1) To 2 c.c. of Tollen's reagent add a drop of the aldehyde. Reduction takes place even in the cold, but no mirror is formed.

(2) Repeat the experiment using Fehling's solution. Note the absence of reduction.

(3) To 5 c.c. of Schiff's reagent add a drop of benzaldehyde. Add 1 c.c. of aldehyde-free alcohol to hasten the reaction. A pink colour is developed.

[In the case of aldehydes insoluble in water, an alcoholic solution may be used.]

(4) Shake 1 c.c. of the aldehyde with 5 c.c. of a saturated solution of sodium bisulphite. Filter off the crystals of the bisulphite compound and wash with cold alcohol till the crystals become odourless. Dissolve the crystals in 5 c.c. of hot water and divide the solution into two parts. To one part add dilute sodium carbonate solution (10%) till there is no further reaction. Benzaldehyde separates and is recognised by its smell.

To the other part add dilute sulphuric acid. The aldehyde is once again liberated along with evolution of sulphur dioxide.

(5) Dissolve four drops of the aldehyde in 10 c.c. of dilute alcohol (1:1). Add four drops of pure phenyl hydrazine and heat to boiling for a few seconds. A bulky crystalline precipitate of the phenyl hydrazone is obtained on cooling. Filter, recrystallise from alcohol (1:1) and determine its melting point. Benzaldehyde-phenylhydrazone melts at  $156^{\circ}$ .

N.B. If phenylhydrazine is not available use a solution of 0.2 g. of phenylhydrazine hydrochloride, 1 g. crystalline sodium acetate in 3 c.c. water.

(6) Heat five drops of freshly distilled aniline with five drops of the pure aldehyde in a test-tube on a water-bath for ten minutes. Pour the liquid on to a watch glass, remove the water carefully with a piece of filter paper, add a small bit of ice and stir with a glass rod. The oily mass goes to a solid and can be filtered. Dry the product on porous tile, recrystallise from 2 c.c. of petroleum ether and find the melting point. Benzylidene aniline melts at  $72^{\circ}$ .

### Ketones

The typical reactions of the keto group are :—

1. Absence of reduction with Tollen's and Fehling's reagents.
2. Formation of oximes and phenyl hydrazones.
3. Reactivity with 2:4 Dinitro-phenylhydrazine as evidence for carbonyl group.

### Acetone

A colourless mobile liquid, miscible with water, alcohol and ether in all proportions, b.p.  $56.5^{\circ}$ .

(1) Carry out the reactions as in the case of aldehydes using (a) Schiff's reagent, (b) Tollen's reagent, (c) Fehling's solution and (d) dilute caustic soda. Acetone and ketones in general differ from aldehydes in not responding to the above tests and are thus distinguished from them.

(2) Mix 5 c.c. of a saturated solution of freshly prepared bisulphite with 5 c.c. of acetone in a test-tube and shake vigorously. On cooling, the bisulphite compound of acetone is thrown down as a crystalline precipitate. The precipitate is filtered and the acetone recovered from the bisulphite compound by distilling with sodium carbonate solution.

(3) To 1 c.c. of water add three drops of acetone and then two drops of a concentrated solution of iodine in potassium iodide followed by 10% sodium hydroxide solution added drop by drop. A yellow precipitate of iodoform is obtained even in the cold.

Under the same conditions ethyl alcohol does not give this test in the cold, and hence it serves as a distinguishing test for acetone. Acetone alone, but not ethyl alcohol, gives iodoform when ammonia replaces sodium hydroxide.

(4) (a) *Denige's test.* To 2 c.c. of a 1 per cent. solution of acetone add 2 c.c. of an acid mercuric sulphate solution and heat the test-tube by immersing in a beaker of boiling water. A heavy white precipitate of the double compound— $2\text{HgSO}_4 \cdot 3\text{HgO} \cdot \text{CO}(\text{CH}_3)_2$ —is formed.

(b) Dissolve 0.5 g. of o-nitrobenzaldehyde in about 2 c.c. of acetone, and stir the solution into about 200 c.c. of water containing a little sodium hydroxide. A deep blue colour develops after sometime due to the formation of indigotin.

(5) Dissolve five drops of acetone in 2 c.c. of water. Add to this three drops of a 1 per cent. solution of sodium nitro-prusside (freshly prepared) and then three drops of 10 per cent. sodium hydroxide. Note that an orange colour develops at first. Divide the solution into two parts, keep one for reference and to the other add three drops of glacial acetic acid. The colour changes to a permanent purple, while the original orange colour in the reference tube changes to yellow in about twenty minutes.

(6) In a small flask (50 c.c. capacity) take 1 c.c. of acetone, 4 c.c. of water, 4 c.c. of benzaldehyde, 20 c.c. of alcohol and 5 c.c. of a 10 per cent., solution of sodium hydroxide. Boil gently for 5 minutes, cool and **shake**. Filter the separated crystals, wash with **a little cold alcohol and recrystallise from** 15 c.c. of boiling alcohol. Collect and dry the crystals of Dibenzylideneacetone on a porous plate and determine the melting point. m.p.  $111-112^\circ$ .

(7) To 2 c.c. of Borsche's reagent add four or five drops of acetone and a drop of concentrated hydrochloric acid and boil for about three minutes. Dilute with water till a turbidity or precipitate appears and warm again till a clear solution is obtained. On cooling, crystals of the yellow dinitrophenyl-hydrazone are obtained. Filter and recrystallise from alcohol (1 c.c.) and determine the melting point ( $128^\circ$ ).

### Acetophenone

A colourless liquid with a characteristic pleasant smell, almost insoluble in water, b.p.  $202^{\circ}$ .

(1) *Colour reactions with sodium nitro-prusside.* Repeat exactly as under acetone, filtering the aqueous solution of the ketone before testing. At first a red colour is developed. On acidifying with acetic acid, a strong blue colour appears which persists even after twenty minutes. The formation of this blue colour is very characteristic and distinguishes acetophenone from acetone.

(2) Repeat experiment (2) as under acetone. No crystalline precipitate is obtained. Acetophenone does not form a bisulphite compound.

(3) Mix 0.5 g. of semicarbazide hydrochloride with 1 g. of sodium acetate crystals and dissolve in 2 c.c. of warm water. Add 0.5 g. of acetophenone (ten drops) and alcohol drop by drop till a clear solution is obtained while hot. Heat for a few minutes and cool. The semicarbazone is deposited as colourless crystals. Filter and determine the melting point. (m.p.  $198^{\circ}$ ).

(4) To 1 c.c. of Borsche's reagent add two drops of acetophenone and a drop of concentrated hydrochloric acid. Warm for two minutes and cool. Crystals of the orange dinitrophenyl-hydrazone separate. Filter, dry and determine the melting point (m.p.  $237^{\circ}$ ).

### Phenols

The characteristic reactions of phenols are :—

1. Insolubility in solutions of sodium carbonate or bicarbonate.
2. Colour reactions with neutral ferric chloride.
3. Reducing action with silver nitrate in the case of higher phenols.
4. Fusion with phthalic anhydride giving rise to phthalein dyes.
5. Benzoylation by the Schotten-Baumann method.

**Phenol.** Colourless crystals becoming reddish and deliquescent on exposure to light and air ; causes powerful blisters when it comes into contact with the skin ; fairly soluble in water, m.p.  $43^{\circ}$  ; b.p.  $183^{\circ}$ .

Use a 10 per cent solution (1 c.c. of liquid phenol and 9 c.c. of water) for the reactions.

(1) To four or five drops of melted phenol, add sodium hydroxide solution (bench reagent, 2N) drop by drop and shake. The phenol dissolves showing that it is acidic. Saturate the solution with carbon dioxide. The phenol is set free, as the compound formed (sodium phenate) decomposes into phenol and sodium carbonate. Phenol is not so strongly acidic as to be soluble in sodium carbonate, and this affords a means of separating it from organic acids.

(2) Add two drops of a neutral ferric chloride solution to 2 c.c. of the aqueous solution of phenol. A violet colour is produced which disappears on adding dilute hydrochloric acid, acetic acid or even alkalis.

(3) *Bromination.* To 2 c.c. of the aqueous solution taken in a test-tube ( $6'' \times 1''$ ) add a saturated aqueous solution of bromine till the colour of bromine is permanent. Collect the white precipitate, suspend it in a little water (5 c.c.) and add a solution of sodium bisulphite till there is a strong smell of sulphur dioxide. Filter again, wash with water, dissolve in a little hot alcohol and add water till a faint turbidity appears and set aside to crystallise. Determine the melting point of the crystals of *s*-tribromophenol ( $93^\circ$ ).

(4) *Liebermann's reaction.* To two drops of melted phenol, add a crystal of sodium nitrite, heat gently and after cooling add 5 drops of concentrated sulphuric acid. A deep blue solution is formed. Pour this into plenty of water (100 c.c.) ; the solution turns red and on adding excess of alkali, becomes blue or green.

(5) *Phthalein fusion.* In a test-tube ( $6'' \times \frac{5}{8}''$ ) place two drops of phenol and add an equal weight of phthalic anhydride. Mix well and add two drops of concentrated sulphuric acid. Heat directly or preferably on a paraffin or sulphuric acid bath at  $160^\circ$  for a few minutes. Then add 2 c.c. of cold water and 10% sodium hydroxide drop by drop till the solution is alkaline. An intense red solution due to the formation of phenolphthalein is obtained.

(6) *Schotten-Baumann reaction.* Dissolve 0.5 g. of phenol in 5 c.c. of water contained in a test-tube, ( $6'' \times 1''$ ) add half a c.c. of benzoyl chloride and then 10% sodium hydroxide solution till it is strongly alkaline. Cork the test-tube and shake vigorously. Cool under the tap, pour the oily product into plenty of water and

rub with a glass rod to induce crystallisation. Filter, wash with plenty of water containing a little alkali and finally with water ; recrystallise the solid from 50 per cent. alcohol. Determine the melting point of the crystals of phenyl benzoate (68-69°).

(7) Dissolve 2 drops of (melted) phenol in 1 c.c. of concentrated sulphuric acid and add the solution slowly to 2 c.c. of a mixture of equal volumes of concentrated sulphuric and nitric acids with cooling. Heat the mixture by immersing in a beaker of boiling water for 15 minutes, cool and pour into 20 c.c. of cold water contained in a beaker. Collect the precipitated picric acid, wash with water and recrystallise from 10 c.c. of water containing 1 c.c. of concentrated hydrochloric acid. Determine the melting point (122.5°).

(8) *Phenoxyacetic acid* : Take 1 g. of phenol in an ordinary test-tube (6" × 1"), dissolve it in 3.5 c.c. of 33 per cent. sodium hydroxide and add 2.5 c.c. of a 50 per cent. solution of monochloroacetic acid. If necessary, add a little water to get a clear solution. Heat the tube loosely stoppered, on a boiling water-bath for about 30 minutes, cool and add dilute hydrochloric acid till the solution is acidic to congo red. Transfer the solution to a small dropping funnel (50 c.c.) and extract twice with 10 c.c. of ether. Remove the aqueous layer and wash the ether layer once with water. Extract the phenoxyacetic acid in the ether layer twice with 5 c.c. of dilute sodium carbonate solution (N) and acidify the sodium carbonate extract with dilute hydrochloric acid (4N). The acid is precipitated. Recrystallise the acid from 6 to 7 c.c. of hot water (m.p. 99°).

(9) *Formation of resins*. Place in a crucible 1 g. of hexamine (p.60), add an equal amount of phenol, and mix intimately with a glass rod. Heat very gently the crucible without allowing charring to take place. A resin is formed which is pliable enough while warm to be moulded easily.

The experiment may be repeated using urea instead of hexamine.

### Catechol

$C_6H_4(OH)_2$  (1 : 2) white crystalline solid easily soluble in water, m.p. 104°. Use an aqueous solution for the following :

(1) To 3 c.c. of an aqueous solution add excess of 2N sodium hydroxide and shake well with air. The solution turns green, then brown and finally black.



(2) To 3 c.c. of the aqueous solution add lead acetate solution. A white precipitate of the lead salt is obtained.

(3) Dissolve 0.05 g. in 10 c.c. of water and to 5 c.c. of this solution add ferric chloride drop by drop. An emerald green colour is noticed at first which changes to violet-red on adding sodium carbonate solution.

(4) To 2 c.c. of the cold solution add ammoniacal silver nitrate. A black precipitate of metallic silver is obtained.

(5) Add 2 c.c. of Fehling's solution to the aqueous solution and heat. Reduction takes place with production of cuprous oxide.

(6) Dissolve 0.15 g. of the substance in 8 c.c. of chloroform. Add 1.2 c.c. of bromine and evaporate to dryness on a water-bath. Dissolve the residue in alcohol (10 c.c.) and precipitate by adding water. Filter, wash with cold water and purify by dissolving again in alcohol and precipitating by addition of water as before. Determine the melting point of the dry product (tetrabromocatechol, m.p. 192-193°; not very sharp, softening commences even at 185°).

(7) Repeat experiment (5) as under Phenol. Alizarin is formed with production of an intense blue solution.

### Hydroquinone

$C_6H_4(OH)_2$  (1 : 4). Soluble in water, alcohol and ether m.p. 169°.

(1) Make an aqueous solution of 0.1 g. of the substance in 5 c.c. of water. To 1 c.c. of the aqueous solution add 2 c.c. of Fehling's solution and warm. Reduction takes place with formation of cuprous oxide.

(2) Carry out the phthalein fusion as described under phenol. A purple colour is developed on pouring the melt into water and making alkaline with sodium hydroxide.

(3) Dissolve 0.2 g. of the substance in 5 c.c. of warm water. Add 2 c.c. of a solution of ferric alum (1 g. in 3 c.c. of water) drop by drop. Cool and shake. Filter the greenish black shining crystals of quinhydrone which separate, wash with 2 c.c. of ice water, dry on porous plate and determine the melting point. On heating it softens and finally melts to a dark orange red liquid at about 170°.

(4) Dissolve 0.8 g. of hydroquinone in 5 c.c. water in a flask (50 c.c.) add methyl sulphate (2 c.c.) which has been freshly washed with ice water in a separating funnel, shake and add caustic soda (2N) drop by drop till there is excess of alkali. Close the flask with a cork and shake vigorously. The dimethyl ether which separates as an oil solidifies on cooling and rubbing the oil with dilute alkali. Crystallise from 50 per cent alcohol. The substance crystallises in plates, with a pleasant aroma (m.p.  $56^{\circ}$ ).

(5) To a dilute aqueous solution of hydroquinone add a few drops of neutral ferric chloride. The solution turns yellow due to the formation of quinone, and becomes colourless again on adding a little sulphurous acid solution.

### Resorcinol

$C_6H_4(OH)_2$ , (1 : 3) white crystalline solid easily soluble in water and alcohol, insoluble in chloroform, m.p.  $118^{\circ}$ .

(1) Carry out the fusion with phthalic anhydride as described under phenol and pour into sodium hydroxide solution. An intense greenish yellow fluorescence is produced.

(2) Dissolve 0.1 g. of the substance in 1 c.c. of concentrated sulphuric acid. Mix in another test-tube 1 c.c. of concentrated sulphuric acid with 1 c.c. of concentrated nitric acid, cool the mixture in ice and add slowly the solution of the resorcinol in concentrated sulphuric acid. Keep the test-tube for a few minutes in ice water. Pour the mixture with the solid into 10 c.c. of cold water containing pieces of ice. Filter the precipitated solid, wash with cold water and recrystallise from dilute alcohol (7 c.c. water and 3 c.c. alcohol) to which a few drops of concentrated hydrochloric acid have been added. Dry the crystals at  $100^{\circ}$  and determine the melting point. The product is trinitroresorcin (m.p.  $175^{\circ}$ ).

(3) Add a few drops of ferric chloride solution to a dilute solution of resorcinol. A blue-violet colour is developed.

(4) Boil 0.05 g. of resorcinol with 5 c.c. of 10% sodium hydroxide solution and a few drops of chloroform. The solution turns red exhibiting fluorescence.

(5) *Tribromo-resorcinol*. Preparation as in (3) p. 66 using 1 g. of resorcinol dissolved in minimum amount of water. (m.p.  $112^{\circ}$ ).

**Pyrogallol**

$C_6H_3(OH)_3$  (1 : 2 : 3). White crystalline solid easily soluble in water, with difficulty in alcohol and ether ; m.p.  $131^\circ$ . Use 1% aqueous solution unless otherwise stated.

(1) *Reaction with ferric chloride* : a fine blue colour which gradually fades is developed.

(2) *Action of alkali* : a deep brown colour is produced on shaking with air.

(3) To 2 c.c. of the aqueous solution add silver nitrate. An immediate dark brown precipitate of metallic silver is formed.

(4) Phthalein fusion : gallein is produced.

(5) Repeat experiment (2) as under Glycerol.

(6) Prepare the triacetate using 0.5 g. of pyrogallol, 2.5 g. of anhydrous sodium acetate and 4 c.c. of acetic anhydride. Crystallise from alcohol or benzene. (m.p.  $160.5^\circ$ )

**Phloroglucinol**

$C_6H_3(OH)_3 \cdot 2H_2O$  (1 : 3 : 5) +  $2H_2O$ , loses water at  $100^\circ$ , soluble in water.

(1) *Reaction with ferric chloride* : a transient violet colour is obtained.

(2) Dip a match stick (pine wood) in concentrated hydrochloric acid and then into an aqueous solution of the phenol. A deep red colour is produced.

(3) To 2 c.c. of an aqueous solution, add a solution of sodium nitrite and a solution of aniline nitrate. A cinnabar red precipitate of benzene-azo-phloroglucinol is obtained.

(4) Dissolve 0.1 g. of phenol in 1 c.c. of concentrated sulphuric acid and pour the clear solution into a mixture of 1 c.c. each of concentrated sulphuric and nitric acids cooled in ice water. Keep the mixture stirred till a precipitate is obtained and then for a further period of 5 minutes. Pour into ice water, filter the precipitate and wash with water containing hydrochloric acid (2 c.c. of water + 0.5 c.c. acid). Recrystallise the trinitrocompound from a boiling mixture of 3 c.c. of water and 1 c.c. of concentrated hydrochloric acid, (m.p.  $165-166^\circ$ ).

 **$\alpha$ -Naphthol**

Colourless crystals with a faint phenolic odour, turning reddish on exposure to light and air ; very sparingly soluble in water (less than  $\beta$ -naphthol); m.p.  $94^\circ$ .

Dissolve 1 g. of  $\alpha$ -naphthol in 10 c.c. of alcohol, dilute it to 25 c.c. with water and use this solution for the reactions.

(1) To 2 c.c. of the solution of  $\alpha$ -naphthol add a few drops of ferric chloride. A *flocculent white* precipitate of di- $\alpha$ -naphthol is thrown down.

(2) Add a few drops of a freshly prepared solution of sodium hypochlorite to 5 c.c. of the naphthol solution. A green colour is produced at first which changes to blue on further addition of the hypochlorite.

(3) Add a saturated alcoholic solution of picric acid to a cold solution of  $\alpha$ -naphthol in alcohol. Orange crystals of the picrate separate out. Filter, wash with a little cold alcohol and determine melting point (m.p.  $189^{\circ}$ ).

(4) Dissolve 0.5 g. of  $\alpha$ -naphthol in 2 c.c. concentrated sulphuric acid and add the solution slowly to a cold mixture of 2 c.c. each of concentrated sulphuric and nitric acids. Heat the mixture on the water-bath for 10 minutes, cool and pour into 50 c.c. of cold water contained in a beaker. Crystallise the yellow precipitate from a little boiling glacial acetic acid diluted with water, and determine the melting point of the crystals. 2:4-dinitro- $\alpha$ -naphthol forms bright yellow needles (m.p.  $138^{\circ}$ ).

(5) 2 : 4 *Dibromo  $\alpha$ -naphthol*. Dissolve 0.5 c.c. of liquid bromine in 1 c.c. of glacial acetic acid. Add 0.25 g. of pure  $\alpha$ -naphthol and warm on the water bath for about 10 min. Pour the mixture into water, when the dibromo compound separates as a white solid. Filter and crystallise from dilute alcohol. (m.p.  $105^{\circ}$ ).

### $\beta$ -Naphthol

Colourless plates, soluble in hot water, m.p.  $122^{\circ}$ .

(1) Dissolve 0.05 g. of the naphthol (a pinch will do) in 10 c.c. of 10% sodium hydroxide, add five drops of chloroform and boil. At first the colour is blue, but it fades rapidly, becomes yellow and finally colourless.

(2) To a warm aqueous solution of  $\beta$ -Naphthol, add a few drops of ferric chloride solution. No colour develops but only a white *opalescence* is observed.

(3) Dissolve four drops of aniline in 1 c.c. of water containing two drops of concentrated sulphuric acid, cool the solution in ice

water and add slowly with shaking 2 c.c. of 10% sodium nitrite. After two or three minutes add 2 c.c. of sodium acetate solution and pour the mixture into a solution of  $\beta$ -naphthol (0.2 g.) in 4 c.c. of 10% sodium hydroxide. A scarlet red precipitate of benzene azo- $\beta$ -naphthol is obtained. (This can be recrystallised from alcohol ; scarlet needles m.p.  $133^{\circ}$ ).

(4) Dissolve 0.1 g. of  $\beta$ -naphthol and 0.15 g. of picric acid in 6 c.c. of boiling alcohol (1:1). On cooling slowly, orange crystals of the picrate appear. Filter and wash with 2 c.c. of dilute alcohol (1 : 1). Dry the picrate and determine its melting point ( $156^{\circ}$ ).

(5)  *$\beta$ -Naphthyl-methyl ether*. To 0.1 g. of  $\beta$ -naphthol contained in a test-tube add 2 c.c. of sodium hydroxide (2N) and half a c.c. of dimethyl sulphate. Cork the test-tube, shake vigorously and warm on a water-bath to destroy the excess of dimethyl sulphate. Filter off the solid which separates on cooling, wash with a little alkali (1 c.c.) then with water and crystallise from 2 c.c. of alcohol. It is white crystalline substance with a very pleasant smell (m.p.  $72^{\circ}$ ).

### Acids

The typical reactions of acids are :—

1. Solubility in bicarbonate solution.
2. Formation of esters with alcohols.
3. Formation of acid chlorides, amides and anilides or toluidides.

#### Formic acid

A colourless liquid with a pungent odour, miscible with water in all proportions, b.p.  $101^{\circ}$ .

Except when specially indicated, use a dilute solution of the acid (3.5%).

(1) To 2 c.c. of concentrated sulphuric acid contained in a small test-tube ( $4'' \times \frac{1}{2}''$ ) add strong formic acid (commercial 90%) drop by drop. Gently warm the test-tube and set fire to the gas. Carbon monoxide is formed which burns with a blue flame.

(2) Take 5 c.c. of the dilute solution in a test-tube ; add ammonia drop by drop till the solution smells slightly ammoniacal. Boil off the excess of ammonia, cool and add to one part ferric chlo-

ride. A red colour is formed which is easily discharged by dilute hydrochloric acid. To the other part add silver nitrate. A white precipitate of the formate is formed which is reduced to black metallic silver after some time.

(3) To 5 c.c. of the dilute solution add 2 c.c. of mercuric chloride and gradually heat the solution to boiling. A white precipitate of mercurous chloride is obtained slowly.

(4) To 4 c.c. of the dilute solution add about 0.3 g. of mercuric oxide, shake well and filter the undissolved oxide. On boiling the solution, a white precipitate of mercurous formate is formed quickly changing to a grey precipitate of metallic mercury.

(5) Heat 0.5 g. of dry sodium formate in a hard glass test-tube fitted with a cork and a delivery tube ending in a jet. Hydrogen is given off and may be lighted at the jet. The residue in the test-tube contains sodium oxalate and sodium carbonate. Dissolve it in a little hot water, filter, neutralise with HCl and test for oxalates as under experiments (2) and (4) for oxalates (p. 74).

### Acetic acid

A colourless liquid with a penetrating odour b.p.  $118^{\circ}$ .

(1) Using 2 c.c. of the dilute acid (2N) repeat experiments (2), (3) and (4) as under formic acid. No reduction is observed as in the case of formic acid.

(2) To a mixture of 2 c.c. of glacial acetic acid and 1 c.c. of water add a few crystals of chromic acid and heat to boiling. No sign of oxidation is noticed.

(3) To a solution of sodium acetate (2N) add ferric chloride till a bright red colour is produced. Divide the solution into two parts. To one add dilute hydrochloric acid drop by drop. The red colour is discharged changing to the yellow colour of ferric chloride.

Boil the remainder of the solution. A precipitate of basic ferric acetate is obtained.

(4) Repeat the test for the formation of ethyl acetate as under alcohol.

(5) Heat 0.2 g. of an acetate with the same weight of arsenious oxide in a hard glass test-tube. Dense fumes with a nauseating odour are given off (cacodyl test : poisonous).

(6) In a test-tube ( $6" \times 5/8"$ ) take 1 g. of freshly fused sodium acetate, add ten drops of strong sulphuric acid, and then 1.5 c.c. of aniline. Fit the tube with a cork carrying a tube about 2 feet long to serve as condenser. Clamp the tube vertically and heat it so that the contents boil gently, for about half an hour. Cool and boil with about 20 c.c. of water in a beaker adding a little decolorising charcoal. Filter hot and set aside to crystallise. Filter the crystals and determine the melting point of acetanilide formed (m.p.  $114^\circ$ ).

### Oxalic acid

$\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$ . A white crystalline solid, soluble in water, loses water of hydration at  $100^\circ$ , the anhydrous acid subliming at  $150-160^\circ$  if slowly heated. Very sparingly soluble in ether. The anhydrous acid melts at  $189^\circ$ .

(1) Heat about 0.5 g. of the acid with 2 c.c. of concentrated sulphuric acid in a test-tube. A mixture of carbon monoxide and carbon dioxide is evolved. If the gases are passed through a little lime-water contained in a test-tube the presence of carbon dioxide is indicated.

Oxalates also behave similarly.

(2) Dissolve a few crystals of the acid or its salt in a little dilute sulphuric acid, warm the solution to about  $60^\circ$ , and add dilute potassium permanganate solution drop by drop. The permanganate is readily decolorised.

(3) Repeat the above experiment adding a little manganese dioxide instead of permanganate. A brisk effervescence due to the evolution of carbon dioxide is noticed.

(4) To a neutral solution of an oxalate (prepared from the acid by neutralising with sodium hydroxide) add calcium chloride. A white precipitate of calcium oxalate is obtained. This precipitate is insoluble in acetic acid but easily soluble in dilute hydrochloric acid.

(5) Take 0.5 g. of the acid in a test-tube and add about 2 grams of para-toluidine. Place the tube on an asbestos board  $4"$  square, supporting it vertically by clamping and heat for about 15 minutes with a micro-burner so that the toluidine vapours are seen condensing. Cool and boil the reaction product with about 15 c.c. of alcohol and filter off the crystallised para-toluidide.

Oxal-para-toluidide crystallises in white crystals (m.p.  $267^\circ$ ).

### Succinic acid

White crystalline solid soluble easily in hot water, difficultly soluble in ether, m.p.  $188^{\circ}$ .

(1) Heat a small quantity of the acid strongly in a test-tube. A white sublimate of the anhydride is obtained and irritating vapours are also evolved.

(2) Neutralise a small amount of the acid (0.1 g.) by adding ammonia in slight excess and boiling off excess of ammonia. Add neutral ferric chloride to the neutral solution. A reddish brown precipitate is obtained of the basic ferric succinate which dissolves easily in dilute hydrochloric acid.

(3) Heat gently a small quantity of the acid (0.5 g.) mixed with twice the weight of resorcinol and four drops of concentrated sulphuric acid till a deep red solution is formed. Pour this into a large volume of water containing a little sodium hydroxide. An intense green fluorescence is obtained.

(4) Preparation of succin-toluidide. Take 0.2 g. of the acid in a dry test-tube ( $6'' \times 5/8''$ ) and mix with 1 g. of para-toluidine. Place the tube in a glycerol-bath such that one-third of the tube is immersed in the liquid and heat for half an hour maintaining the temperature at  $200^{\circ}$ . Cool the tube and boil with 15 c.c. of dilute alcohol. Filter and recrystallise the precipitate from boiling alcohol, and determine the melting point ( $254^{\circ}$ ).

### Lactic acid

Thick syrupy liquid, very soluble in water.

Dissolve a drop of the acid in about 15 c.c. of water and add one or two drops of a 10 per cent. neutral ferric chloride solution. A strong yellow colour is developed.

(2) Distil 1 c.c. of the acid with 5 c.c. of 50 per cent. sulphuric acid in a small flask fitted with a cork and bent tube (vide acetaldehyde preparation) and absorb the product in a little water. Acetaldehyde is formed (test by any of the tests given) and carbon monoxide escapes and can be set fire to.

(3) To 1 c.c. of a 1 or 2 per cent. solution of phenol, add neutral ferric chloride solution till a distinct violet colour is obtained and then add lactic acid in drops. The violet colour changes to yellow.



(4) Carry out the iodoform reaction. Lactic acid also gives the iodoform reaction.

(5) To 5 c.c. of concentrated sulphuric acid containing three drops of a saturated copper sulphate solution, add three or four drops of a 1 per cent. alcoholic solution of lactic acid. Heat on a boiling water-bath for five minutes and add two drops of a 0.2 per cent. alcoholic solution of thiophene. A cherry-red colour is formed on warming.

### **Tartaric acid**

Colourless, transparent, crystalline solid easily soluble in water, m.p. 169°.

A 5 per cent solution of Rochelle salt (sodium potassium tartrate) is used for the tests.

(1) Heat a little of the acid (0.2 g.) or its salt in a dry test-tube. The mass swells up, chars and gives off a smell of burnt sugar.

(2) Repeat the above experiment after adding 1 c.c. of concentrated sulphuric acid. The mixture blackens and sulphur dioxide, carbon monoxide and carbon dioxide are given off.

(3) To a neutral solution of a tartrate (5 c.c.) add 1 c.c. of dilute calcium chloride solution. A white crystalline precipitate of calcium tartrate comes down slowly, and much quicker by gently rubbing the sides of the tube with a glass rod. Filter off the precipitate and divide into two parts. To one part add dilute acetic acid and warm. The calcium tartrate dissolves.

To the other part add dilute sodium hydroxide. The precipitate dissolves in this reagent as well, but on boiling, it is reprecipitated and on cooling, it redissolves.

This reaction is characteristic of tartaric acid.

(4) *Denige's test.* To 2 c.c. of concentrated sulphuric acid containing 2 to 3 drops of a dilute (2%) solution of resorcinol, add two drops of a solution of a tartrate and warm the mixture. A characteristic violet colour is developed due to the formation of glycollic aldehyde.

(5) To a small amount of the acid add ten to fifteen drops of a freshly prepared solution of  $\beta$ -naphthol (0.1 g. in 5 c.c. of concentrated sulphuric acid) and heat on a water-bath till no further change in colour is observed. Add 15 c.c. of water.

Tartaric acid at first produces a blue colour which changes to green and finally becomes reddish yellow.

(6) *Fenton's test.* To 2 c.c. of the neutral tartrate solution add an equal volume of water and not more than two drops of a dilute solution of ferrous sulphate. On adding two drops of hydrogen peroxide (1%), followed immediately by sodium hydroxide an intense violet colour is developed.

(7) *Preparation of the Dianilide.* Take finely powdered tartaric acid (1 g.) in a test-tube (6" × 1") fitted with a cork and a short reflux tube and add 2 c.c. of pure aniline. Heat the mixture to 140-150° in a sulphuric acid bath and keep it at this temperature for half an hour. The mixture first melts and then gradually solidifies due to the formation of the anilide. Cool the tube and boil with sufficient rectified spirits to dissolve the anilide and filter while hot. The sparingly soluble anilide comes out in pure white crystals (m.p. 270°).

### Citric acid

White crystalline solid soluble in water, and alcohol and insoluble in ether. (m.p. of the hydrate 100°, loses water at 130° and melts at 153°).

Use a 5% solution of sodium citrate for the tests.

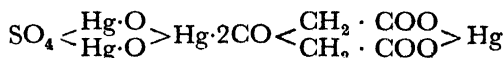
(1) Heat a small quantity of the acid with 1 c.c. of concentrated sulphuric acid. Carbon monoxide and dioxide are given off at first. No blackening is observed due to separation of carbon (cf. Tartaric acid).

To 1 c.c. of a neutral solution of a citrate add calcium chloride solution. No precipitation takes place in the cold. On boiling vigorously a white crystalline precipitate of calcium citrate is produced. A drop of alkali hastens precipitation.

(3) To 5 c.c. of the neutral citrate solution add 1 c.c. of silver nitrate solution. A white precipitate of the citrate of silver is obtained. Add dilute ammonia drop by drop till the precipitate dissolves completely. Place the tube in boiling water for two or three minutes. Reduction does not take place in such a short time as is the case with a tartrate.

(4) *Denige's test.* Add 1 c.c. of Denige's solution to 5 c.c. of the citrate, heat to boiling and then add 2 drops of a 1% solution of potassium permanganate. Decolorisation takes place immediately.

tely followed by the appearance of a heavy white precipitate. This precipitate is a double salt of basic mercuric sulphate and mercuric acetone dicarboxylate having the following formula :



(5) *Colour reaction.* Repeat experiment (5) as under tartaric acid. The colour is intense blue at first and becomes finally pale green permanently. On adding water, the colour changes to orange-yellow.

### Benzoic acid

White shining leaflets with a peculiar characteristic smell, nearly insoluble in cold water but readily dissolving in hot water, alcohol and ether ; on heating it sublimates readily, m.p. 121-122°.

Dissolve 0.5 g. of the acid in a slight excess of ammonia (4N), boil off excess of the ammonia and dilute to 20 c.c. Use this solution for the reactions.

(1) To 5 c.c. of the above neutral solution add ferric chloride (neutral). A flesh coloured precipitate of a basic ferric benzoate is obtained. On adding dilute hydrochloric acid, the benzoate is decomposed with separation of benzoic acid.

(2) To 5 c.c. of the neutral benzoate solution add silver nitrate. A white precipitate of the silver salt is obtained which dissolves readily in hot water.

(3) To 0.1 g. of the acid add 1 c.c. of alcohol and 5 drops of concentrated sulphuric acid. Warm for a few minutes and pour into dilute sodium carbonate solution contained in a dish. A fragrant smell due to ethyl benzoate is perceived.

(4) Mix in a mortar 1 g. of benzoic acid with four grams of dry-soda lime. Place the mixture in a hard glass test-tube (5" × ½") fitted with a one-holed cork and bent tube, place a layer of pure soda-lime 1 cm. thick above the mixture and clamp the tube horizontally. The bent tube dips into a test-tube immersed in cold water. Heat the layer of soda-lime strongly and extend the heat to the layer of the mixture. Drops of benzene mixed with water collect in the tube. Dry the liquid with calcium chloride and determine its boiling point.

(5) *Benzenesulphide.* To about 0.2 g. of the acid in a dry test-tube add twice the weight of phosphorus pentachloride.

Warm the tube while stirring the contents until a homogeneous liquid is obtained. Cool and shake with cold water to decompose the excess of the phosphorus halide and pour off the aqueous layer. Add 1 c.c. aniline slowly drop by drop and shake. Boil the reaction product with 10 c.c. of dilute alcohol and filter when crystals of benzanilide separate out. Determine the melting point. (m.p. 159-160°).

### Cinnamic acid

Colourless solid crystallising in plates, very slightly soluble in cold water but easily in hot water, soluble in alcohol m.p. 133°.

(1) Dissolve 0.1 g. of the acid in carbon tetrachloride (1 c.c.) and add drop by drop a solution of aniline in the same solvent. Warm gently. Decolorisation occurs, showing that the acid is unsaturated.

(2) In a test-tube the acid (0.1 g.) with about 5 c.c. of a strong solution of potassium permanganate. The smell of benzaldehyde is noticed.

(3) Add 0.2 g. of the acid to 10 c.c. of fuming nitric acid (sp. gr. 1.5) contained in a crystallising basin with stirring. The acid slowly dissolves and a light coloured precipitate gradually separates out. Set aside for about fifteen minutes and then add 40 c.c. of water with constant stirring. Filter the precipitate, wash with a little ether and crystallise from boiling alcohol. The substance is para-nitrocinnamic acid (m.p. 287°).

### Phthalic acid

Colourless solid crystallising in plates, soluble in water and in alcohol (d. 1.5°).

(1) Repeat the fluorescein test as under succinic acid.

(2) To 0.2 g. of the acid contained in a test-tube fitted with refluxing arrangement, add 1 c.c. of aniline. Heat with a micro-burner on an asbestos sheet for about twenty minutes. Boil the reaction product with 10 c.c. of alcohol 1:1, filter and recrystallise from alcohol.

Phthalanil,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ < \\ \text{CO} \end{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_5$  (m.p. 204—205°) is formed.

(3) Repeat experiment (4) under benzoic acid and show formation of benzene.

### Salicylic acid

White crystalline solid (needle shaped crystals) soluble in hot water easily and also in alcohol, m.p. 157°.

(1) Add neutral ferric chloride solution to a saturated aqueous solution of the acid. A purple colour is developed, discharged by hydrochloric acid but not by acetic acid.

(2) Apply the wintergreen oil test as under methyl alcohol.

(3) Place a layer of 2 cm. of good soda-lime mixed with 0.1 g. of the acid in a test-tube (16"  $\times$  5/8") and further up another centimeter layer of soda-lime. Draw out near the mouth of the test-tube so as to form a neck. Heat the closed end of the tube gradually as well as the soda-lime and collect the phenol in another tube. Prepare phenol as under phenol.

(4) Dissolve 0.2 g. of the acid in 5 c.c. of boiling water. Add 2 c.c. of nitric acid (sp. gr. 1.4) and boil gently for about ten minutes. Pour into cold water (20 c.c.). Filter the precipitate, wash with water and dry from boiling water. 5-Nitro-salicylic acid is obtained (m.p. 26°).

(5) To a solution of 0.2 g. of the acid in 2 c.c. dilute HCl, add 3 to 4 c.c. of saturated bromine water. A white crystalline precipitate of 3 : 5 dibromosalicylic acid is obtained. (m.p. 218°).

### Gallic acid

$C_6H_2CO_2H(OH)_3$  (1:3:4:5), m.p. 220° d; soluble in hot water, easily in alcohol and ether.

(1) To 1 c.c. of an aqueous solution add ferric chloride. A blue-black precipitate is obtained.

(2) To 1 c.c. of the solution add lime-water. A blue colour is formed at first and with excess of lime-water a blue precipitate is obtained.

(3) To 1 c.c. of the solution add an equal volume of 1% gelatin solution. No coagulation takes place.

(4) To 2 c.c. of the solution add an equal volume of cold saturated ferrous sulphate. No coloration is produced at first, but on standing the solution turns deep blue.

(5) Warm 0.1 g. of the acid with 0.5 c.c. of concentrated sulphuric acid, the solution becomes green and then deep red on pouring into dilute alkali a blue solution is obtained.

### Esters

These are usually pleasant smelling liquids or solids of low melting point insoluble in water. They are identified only by the products of hydrolysis. In many cases a solution of sodium or potassium hydroxide (20 to 30 per cent) works satisfactorily while in others a mixture of equal volumes of water and sulphuric acid is found to be more suitable for the hydrolysis. The time taken for hydrolysis varies with the nature of the ester : the esters of oxalic acid are hydrolysed in a few minutes while other esters may take one to two hours.

#### Ethyl oxalate

A colourless liquid with a faint ethereal smell, b.p. 185°.

(1) To 1 c.c. of the ester add drop by drop a 15 per cent solution of sodium hydroxide till the layer of ester has disappeared, and shake. A white precipitate of sodium oxalate separates at once. Filter the precipitate and test for oxalate by experiments (2), (3) and (4) (p. 74).

(2) To  $\frac{1}{2}$  c.c. of the ester add a few drops of alcohol and 1 c.c. of strong ammonia and shake. A white precipitate of oxamide is obtained at once. It melts above 300° (m.p. 418°).

#### Ethyl acetate

A colourless liquid with an agreeable fruity odour, slightly soluble in water, b.p. 77°.

In a 100 c.c. round bottom flask, take 5 c.c. of ethyl acetate and 30 c.c. of 25% sodium hydroxide. Fit the flask with a reflux condenser, add two pieces of porous porcelain to prevent bumping and reflux for about half an hour by which time the oily layer disappears. Cool the flask, replace the condenser by a small fractionating column to which a small water condenser is attached and distil, collecting about 5 c.c. of the liquid in a test-tube.

With  $\frac{1}{2}$  c.c. of the distillate, carry out the iodoform reaction.

Saturate the rest of the distillate with anhydrous potassium carbonate to get the pure alcohol and withdraw the liquid by a pipette. With a few drops of the alcohol carry out a boiling point determination ; with the remainder prepare the 3 : 5, dinitro-benzoate of the alcohol as described in detail under methyl alcohol.

Neutralise the liquid remaining in the distilling flask with hydrochloric acid (1:1) and evaporate to dryness on a water-bath. Take in a test-tube fitted with reflux arrangement 1 g. of the residue, add 1 c.c. of concentrated hydrochloric acid and then 1 g. of p-toluidine and heat on asbestos board for about one hour ; cool and extract the residue with 5 c.c. of boiling absolute alcohol till nothing but white sodium chloride remains. Filter hot and pour into water (50 c.c.). A resinous mass separates along with the p-toluidide. Evaporate the whole of the liquid to about 10 c.c. and filter hot. On cooling and shaking vigorously crystals of the aceto-p-toluidide separate out (m.p.  $148^{\circ}$ ).

This procedure is very useful for identifying acids which are soluble in water and are therefore not precipitated on acidifying.

### Ethyl benzoate

A colourless, sweet-smelling oil, b.p.  $211^{\circ}$ .

Repeat the above experiment using 3 c.c. of ethyl benzoate and 20 c.c. of 25% sodium hydroxide. Alcohol is separated exactly as described in the previous experiment.

On acidifying the residue with dilute sulphuric acid benzoic acid is precipitated, which is filtered and identified by its melting point and preparing its anilide as described under benzoic acid.

### Benzyl benzoate

A colourless liquid with a faint odour, b.p.  $323^{\circ}$ .

Carry out the hydrolysis of 3 g. of the ester with 20 c.c. of 25% sodium hydroxide in a round bottom flask using a reflux condenser. Note that the oily layer does not disappear even after boiling for a long time (2 hours), although the odour of the ester has completely disappeared. Pour the contents into a separating funnel and extract twice with ether. Dry the ether extract over anhydrous potassium carbonate and distil off the ether from a hot water-bath. The residual liquid is benzyl alcohol. Identify by—

- (1) determining its boiling point ;
- (2) treating with a pellet of sodium ;
- (3) oxidising it to benzaldehyde, or benzoic acid ;

(as described under benzyl alcohol)

to obtain the acid, proceed as with ethyl benzoate.

### Ethers

Ethers are a group of bodies which are non-reactive and approach therefore the hydrocarbons as regards chemical properties. There are two types of ethers to be considered—

- (1) aliphatic ethers,
- (2) aliphatic-aromatic ethers (phenolic ethers) like anisole and phenetole.

**Aliphatic ethers.** Use isoamyl ether or pure diethyl ether free from moisture and alcohol.

(1) To a few drops of pure isoamyl ether add a clean bit of sodium. See if there is any gas evolution. If bubbles of gas are seen to come off, wait till they have disappeared and observe that the sodium is practically unchanged.

(2) Add a few granules of phosphorous pentachloride. No reaction takes place.

(3) To 2 c.c. of ice-cold concentrated sulphuric acid contained in a test-tube add 1 c.c. of the ether. Shake the test-tube gently while keeping it immersed in a bath of ice water. The ether dissolves forming a clear solution. Pour the solution into another tube containing 3-4 c.c. of cold water. Note the appearance of two layers. Withdraw the upper layer by a long pipette into another test-tube, wash with 5 c.c. of sodium carbonate solution and separate the upper layer once again by means of the pipette. Dry the liquid with solid potassium carbonate and determine the boiling point of the liquid. It will be the same as that of the original liquid, showing that no change had taken place.

(4) *Formation of 3:5, dinitro-benzoates from simple aliphatic ethers.* To 1 c.c. of isoamyl ether add 0.2 g. of freshly fused zinc chloride and 0.5 g. of 3:5, dinitro-benzoyl chloride and reflux gently by heating in a glycerol bath. After an hour, pour the reaction product into 10 c.c. of sodium carbonate solution (N/2) contained in a small beaker, wash the tube with 2 c.c. more of the carbonate solution and filter after five minutes, wash the solid ester with a little carbonate and finally with water. Recrystallise the ester from 2-3 c.c. of carbon tetrachloride and find its m.p.



**Aromatic ethers.** Use **Anisole** b.p.  $154^{\circ}$ .

Take 1 c.c. of anisole in a test-tube ( $6'' \times 1''$ ) fitted with a long tube ( $2'$ ) bent twice at right angles (Fig. 38) and connected to a small test-tube with a side-tube, add 5 c.c. of concentrated hydriodic acid (sp. gr. 1.8) free from iodine and place in the small test-tube a little alcoholic silver nitrate (1 c.c.). Place the tube in a glycerine bath and gradually raise the temperature till it comes to about  $130^{\circ}$ . Methyl iodide is formed and reacts with the silver nitrate producing a precipitate of silver iodide. Heat for about 30 minutes. Then cool the tube, add sufficient sodium hydroxide to completely dissolve the hydriodic acid and phenol and separate from any unattacked ether. Then acidify with dilute HCl and extract twice with ether. Drive off the ether and prepare the bromo-derivative of the residual phenol and determine its melting point. Anhydrous aluminium chloride or aluminium bromide can also be used to decompose ethers but hydriodic acid is more convenient.

**2 : 4 Dinitro-anisole.** Dissolve 1 c.c. of the liquid in 5 c.c. of concentrated sulphuric acid. Add 1 c.c. of concentrated nitric acid a few drops at a time, while cooling at intervals. Keep for 10 minutes, pour into ice water and shake. Filter, wash with water and crystallise from a small quantity of alcohol. (m.p.  $86^{\circ}$ ).

### Carbohydrates

These contain hydrogen and oxygen generally in the same proportion as in water and hence their name.

The simplest members are monosaccharides having the empirical formula  $\text{CH}_2\text{O}$  and to this group belong glucose and fructose.

Cane sugar or sucrose and milk sugar or lactose belong to the group of disaccharides.

Starch belongs to the group of polysaccharides with an indefinite formula,  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ .

### General test for carbohydrates

**Molisch's test.** To 2 c.c. of a dilute aqueous solution (0.1 per cent.) of the substance add 2 drops of a 20 per cent. alcoholic solution of *L*-naphthol and then pour carefully 2 c.c. of concentrated sulphuric acid down the side of the tube. A deep violet colour is produced which gradually spreads throughout the liquid. This colour is discharged on adding alkali.

### General reaction for monosaccharides

*Barfoed's reaction.* Add 1 c.c. of Barfoed's reagent to 1 c.c. of the sugar solution (2 per cent) in a test-tube and heat the test-tube by immersion in boiling water. Reduction to red cuprous oxide takes place in 2 minutes if a monosaccharide is present.

### Monosaccharides

#### Glucose

A white crystalline solid, easily soluble in water, difficultly in alcohol ; it is not soluble in ether or other solvents (m.p. 144-146° for anhydrous glucose).

Use a solution of 1 g. in 50 c.c. water for the following tests :—

(1) *Fehling's test.* In a test-tube (6" × 1") prepare 10 c.c. of Fehling's solution (by mixing equal volumes of the copper sulphate and the alkaline-tartrate), heat the solution to boiling and add the glucose solution in drops until the deep blue colour disappears. Red cuprous oxide is precipitated.

(2) Clean a test-tube first with sodium hydroxide to remove grease. Pour off the alkali and wash with water. Add a few c.c. of stannous chloride solution and rotate the tube so that the solution wets the entire tube. Pour off the solution, clean with water, add 10 c.c. of Tollen's reagent and 2 c.c. of the glucose solution and warm the tube by immersion in a beaker of hot water. A silver mirror is produced.

(3) To 0.2 g. of the sugar in a test-tube add concentrated sulphuric acid drop by drop from a pipette, cooling under the tap after each addition. No darkening of the solution takes place. Immerse the tube in a boiling water-bath. The solution becomes dark brown or black.

(4) Mix equal volumes of the sugar solution and N-sodium hydroxide and heat gradually to boiling. The solution turns yellow, and then becomes dark-brown or black with separation of a resinous mass (Cf. aldehyde).

(5) *Condensation with phenyl hydrazine.* To 0.2 g. of glucose dissolved in 10 c.c. of water add 3 c.c. of freshly prepared phenyl hydrazine reagent, (see Appendix) loosely plug the tube with cotton wool and immerse in a beaker of boiling water. In about ten minutes the glucose crystallises out. Filter and

recrystallise from alcohol (m.p.  $205^{\circ}$ ). The yellow crystals seen under the microscope have a characteristic appearance of sheaves of corn.

(6) *Acetylation.* Mix thoroughly 1 g. of glucose and 0.5 g. of freshly fused sodium acetate. Transfer the mixture to a test-tube ( $6 \times 1$ ") fitted with a one-holed stopper and glass tube 2 feet long and add 5 c.c. of pure acetic anhydride and heat on a tiny flame for about an hour. Pour the solution into 30 c.c. of cold water contained in a beaker and stir vigorously. Break up any lumps and keep the crystals in contact with water for sometime to decompose excess of acetic anhydride. Filter the crystals and recrystallise from dilute alcohol or plenty of water. Glucose penta-acetate is obtained (m.p.  $111^{\circ}$ ).

This experiment shows the presence of hydroxyl groups in glucose.

Carry out the reduction tests with a little of the acetyl derivative and note that the aldehyde group is still active.

(7) Boil 5 c.c. of the dilute solution of glucose with 1 c.c. of Nylander's reagent for a few minutes. Reduction takes place with formation of a black precipitate of bismuth. This is a delicate test for glucose.

### Fructose

Pure fructose crystallises from alcohol in needles, very readily soluble in water, and in cold alcohol, m.p.  $95^{\circ}$ . It is very hygroscopic and is usually obtained as a syrup.

(1) Carry out the reductions with Fehling's solution, Tollen's reagent, and Barfoed's reagent, using a 2% solution of the sugar.

(2) *Action of concentrated sulphuric acid.* Repeat experiment as with glucose. At first an orange brown solution is formed in the cold. On warming, at  $100^{\circ}$  the mixture becomes rapidly dark brown or black.

(3) *Action of sodium hydroxide.* Repeat experiment as with glucose. Fructose becomes brown rather more rapidly than glucose.

(4) *Osazone test.* Carry out the reaction exactly as described under glucose. The osazone is formed much more readily and in a shorter time. It is identical with glucosazone. Both glucose and fructose give the same osazone.

(5) *Furfurol test.* Dissolve 0.3 g. of the sugar in 5 c.c. of dilute hydrochloric acid. Boil the solution for a few minutes and place a strip of freshly prepared aniline acetate paper at the mouth of the tube and boil the solution again. The vapours of furfuroil formed act on the aniline acetate paper producing a light red colour.

(6) *Pinoff's test.* To a solution of 0.1 g. of the sugar in a little water add an equal volume of a freshly made 4 per cent. solution of ammonium molybdate and then 4 drops of glacial acetic acid. Heat on a boiling water-bath. In a few minutes a deep blue colour develops.

(7) *Seliwanoff's test.* Boil a few drops of the sugar solution with 5 c.c. of Seliwanoff's reagent. A red precipitate is formed. Glucose gives only a red coloration and not a precipitate after prolonged boiling.

## Disaccharides

### Cane Sugar

A white crystalline solid easily soluble in water and difficultly in alcohol m.p.  $160^{\circ}$ .

Use a 2 per cent solution unless otherwise specified.

(1) To a little of cane sugar or a saturated solution of it add concentrated sulphuric acid; immediate charring takes place. If a warm saturated solution is used, instead of the solid, steam and carbon dioxide are given off and the mass swells up leaving a black carbonaceous mass.

(2) Repeat the experiments for glucose with cane sugar solution, using (a) sodium hydroxide, (b) phenyl hydrazine reagent. No reaction takes place in either case showing the absence of a free aldehyde group.

(3) To 5 c.c. of Fehling's solution add 2 c.c. of cane sugar solution and boil. Reduction takes place.

The reaction is negative also with Tollen's reagent.

(4) Boil 2 c.c. of the sugar solution with 2 c.c. of dilute hydrochloric acid for a minute, cool and then carefully neutralise with sodium hydroxide solution. Add 5 c.c. of Fehling's solution and heat to boiling. Reduction takes place with formation of cuprous oxide.

(5) Repeat experiment (4) using 2 c.c. of N-nitric acid and neutralising with ammonia. Add 5 c.c. of Tollen's reagent and warm. A silver mirror is produced.

In both the cases the cane sugar is hydrolysed to glucose and fructose.

### Lactose

Crystallises with one molecule of water. It is less soluble in water than cane sugar. Insoluble in alcohol, m.p.  $203^{\circ}$  d.

Use a solution of 1 g. of sugar in 50 c.c. of water.

(1) To 0.2 g. of lactose in a test-tube, add concentrated sulphuric acid drop by drop. No change is noticed in the cold. On warming the tube by immersion in a boiling water-bath, decomposition with charring takes place rapidly and the solution becomes greenish black. Carbon dioxide and sulphur dioxide are also evolved.

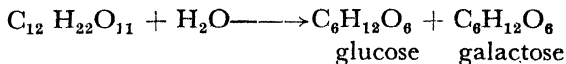
(2) To 5 c.c. of lactose solution add an equal volume of sodium hydroxide and heat to boiling. The reaction is the same as with glucose but takes place more slowly.

Reduction takes place both with Fehling's solution and Tollen's reagent as with glucose.

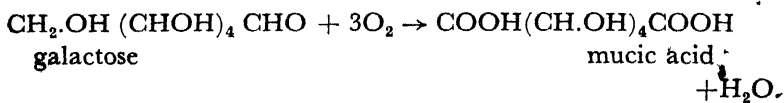
(3) *Barfoed's reagent*. No reduction is observed.

(4) *Osazone test*. Repeat experiment as described under glucose. No precipitation of the osazone takes place in the hot solution. On cooling lactosazone crystallises out. It can be recrystallised from hot water and forms clusters of thin needles (m.p.  $200^{\circ}$  d).

(5) Boil 2 to 3 c.c. of the solution with 2 c.c. of dilute hydrochloric acid for two minutes. Cool the solution, neutralise and carry out the test with Fehling's solution. Reduction takes place much more quickly due to the formation of glucose and galactose as a result of hydrolysis.



(6) *Mucic acid test*. Using 1 g. of lactose prepare mucic acid (see under preparations). Glucose and cane sugar do not answer this test.



### Polysaccharides

**Starch.**  $(C_6H_{10}O_5)_n$ 

A white powdery solid, insoluble in cold water, alcohol and ether. Forms a colloidal solution on boiling with water.

*Starch solution.* Mix 1 g. of soluble starch with 15 c.c. of water in a mortar so as to get a uniform suspension. Meanwhile boil 100 c.c. of water and pour this suspension in a thin stream into the boiling water. Boil for another two minutes and cool.

(1) *Iodine test.* Add two drops of a solution of N-iodine in potassium iodide to 10 c.c. of water, and to this add 10 c.c. of dilute starch solution (1 c.c. of the stronger solution diluted with 9 c.c. of water). A blue solution is obtained. On warming this to  $80^\circ$  the colour disappears but reappears on cooling.

(2) Carry out the Fehling's test with 4 c.c. of starch solution ; hardly any reduction takes place.

To 10 c.c. of starch solution add 4 drops of concentrated hydrochloric acid and heat in a boiling water-bath for about half an hour. Cool to room temperature, neutralise with dilute sodium hydroxide and perform both the Fehling's and the iodine tests. Reduction takes place with formation of cuprous oxide, but no blue colour is obtained with iodine solution.

(3) To 20 c.c. of starch solution add a few c.c. of malt extract, warm to  $40^\circ$  for about twenty minutes and carry out the Fehling's test. (If malt extract is not available, 2 c.c. of fresh saliva may be used.)

Fehling's solution is reduced after this treatment due to the formation of a reducing sugar by the action of the enzymes present in malt (diastase) or in saliva (ptyalin) on the starch.

(4) To 5 c.c. of the starch solution add an equal volume of a saturated solution of ammonium sulphate. Starch is precipitated.

(5) Repeat the above experiment substituting an equal volume of alcohol for the ammonium sulphate. Starch is precipitated even more readily in this case.

## CHAPTER IV

### REACTIONS OF COMPOUNDS CONTAINING OTHER ELEMENTS, e.g., NITROGEN, HALOGENS, SULPHUR, Etc.

#### Amines

**Aliphatic. Primary :** Use a solution of methyl-amine in water or solid methyl-amine hydrochloride (m.p.  $210^{\circ}$ ) :

(1) Heat a little solid methyl-amine hydrochloride with dry soda-lime in a test-tube. Note the fishy ammoniacal odour of methyl-amine. Expose a red litmus paper to the gas and observe its alkaline nature. Set fire to the escaping gas at the end of a jet and note its easy inflammability.

(2) To 2 c.c. of aluminium sulphate solution add an aqueous solution of methyl-amine drop by drop. At first a white precipitate of the hydroxide is obtained which dissolves to a clear solution in excess of the amine solution.

Repeat the experiment using 1 c.c. of cupric sulphate solution. Cupric hydroxide is precipitated at first and dissolves to a deep blue solution in excess of the amine. (Cf.  $\text{NH}_3$ ).

(3) Mix in a test-tube with side-tube ( $6'' \times \frac{1}{2}''$ ), 0.5 g. of the hydrochloride with 1 g. of sodium nitrite and 5 c.c. of water. Nitrogen is given off and can be collected over water in the usual way and tested. Distil about 3 c.c. of the liquid into a second tube. Show the presence of methyl alcohol by oxidation with copper gauze and test for formaldehyde by the resorcin test.

(4) To 1 c.c. of the methyl-amine solution add 2 drops of chloroform and 2 c.c. of alcoholic potash. On gently warming, an offensive odour of methyl carbylamine is produced. Acidify the contents of the tube before pouring into the sink.

(5) *Rimini's test.* To one drop of the solution of methyl amine add 1 c.c. of acetone and 1 drop of a 1 per cent. solution of sodium nitroprusside. A violet-red colour is developed in about a minute. (Distinguishing test for a primary aliphatic amine).

(6) To  $\frac{1}{2}$  c.c. of the solution add 1 c.c. of carbon bisulphide and 1 c.c. of mercuric chloride solution. On boiling, a precipitate

of the sulphide of mercury is obtained and the pungent smell of mustard oil is perceived.

(7) To 0.2 g. of the hydrochloride dissolved in the minimum amount of water add 5 c.c. of a saturated aqueous solution of picric acid. Thoroughly shake and set aside. The picrate of methyl-amine slowly separates in fine yellow needles (m.p.  $207^{\circ}$ ).

**Reactions of secondary amines.** To 1 c.c. of a cold saturated solution of sodium nitrite add 1 g. of diethyl-amine hydrochloride and 1 drop of dilute sulphuric acid. On gently warming the liquid, diethyl nitrosamine collects on the surface as a yellow oil. Extract with 5 c.c. of ether, evaporate the ether and with the residue carry out Liebermann's reaction as described under phenol (p. 66).

**Reactions of tertiary amines.** Use a strong solution of trimethylamine.

(1) Warm the solution and set fire to the gas at the end of a jet. Note the increased luminosity of the flame.

(2) Carry out the reaction with sodium nitrite; observe that no reaction takes place.

(3) Prepare the picrate as under methyl-amine (m.p.  $216^{\circ}$ ).

## Aromatic Amines

### Primary Amines

#### Aniline

A colourless oily liquid when freshly distilled, turning brown on exposure to air; sparingly soluble in water and easily soluble in alcohol and ether; sp. gr. 1.036 at  $0^{\circ}$ , b.p.  $184^{\circ}$ .

Use either the base itself or a saturated aqueous solution of it as indicated.

(1) To three drops of aniline in a test-tube add dilute hydrochloric acid drop by drop. Observe that the aniline dissolves completely forming a salt. Add sodium hydroxide drop by drop; the aniline is reprecipitated as an oil.

*Aniline hydrochloride.* Dissolve five drops of aniline in 2 c.c. of dry ether in a test-tube. Immerse the latter in a beaker of cold water and pass dry hydrogen chloride till no more of it is taken up. A white precipitate of the hydrochloride is obtained. Filter and wash the precipitate with dry ether.



(2) Add a drop of the saturated aqueous solution of aniline to 10 c.c. of water and then a few drops of a filtered solution of bleaching powder or of sodium hypochlorite. A purple coloration slowly appears and finally changes to brown. On adding a drop of ammonium sulphate to the purple solution the colour changes to a rose-red.

(3) Dissolve 2 drops of aniline in 2 c.c. of dilute sulphuric acid and add a few drops of potassium chromate or dichromate solution. The colour changes through green, blue and black and finally a black precipitate is thrown down.

(4) To three drops of aniline add excess of dilute hydrochloric acid and then sodium nitrite drop by drop till free nitrous acid is formed (test a drop with starch iodide paper). On warming the solution a smell of phenol is noticed.

(5) To 5 c.c. of the aqueous solution of aniline contained in a 100 c.c. beaker add saturated bromine water drop by drop till there is a slight excess of it. A copious white precipitate of tri-bromaniline is obtained which settles easily if a piece of ice is added. Filter, wash with water and crystallise from dilute alcohol (m.p.  $116^{\circ}$ ).

(6) *Diazotisation.* Dissolve five drops of aniline in a slight excess of dilute hydrochloric acid, cool in ice water and add sodium nitrite drop by drop till there is a slight excess of the nitrite. Add 1 c.c. of a strong solution of sodium acetate and pour slowly a solution of 0.5 g. of  $\beta$ -naphthol in 1 c.c. of 2N sodium hydroxide. A scarlet precipitate of benzene-azo- $\beta$ -naphthol is formed. Recrystallise from alcohol (m.p.  $133^{\circ}$ ).

(7) *Acetylation.* (a) Add acetyl chloride drop by drop to 1 c.c. of aniline as long as there is an action. Add about 15 c.c. of water, heat to boiling, filter hot and cool. Find the melting point of the crystals of acetanilide which separate (m.p.  $114^{\circ}$ ).

(b) To 0.5 c.c. of aniline emulsified with 2 c.c. water add an equal amount of acetic anhydride and shake. The mixture becomes hot and in a few minutes acetanilide separates out. Recrystallise from hot water.

(8) *Diphenyl urea.* In a boiling tube ( $6'' \times 1''$ ) fitted with a one-holed cork and refluxing arrangement place 1 g. of dry urea and 3 c.c. of aniline and gently boil the contents for twenty minutes. On cooling, the mixture becomes solid. Stir the mix-

ture into 5 c.c. of very dilute hydrochloric acid to remove excess of aniline, filter and crystallise the residue from alcohol. Diphenyl urea melts at  $238^{\circ}$ .

(9) Carry out the carbylamine reaction as under methylamine.

### Secondary amines

#### Methylaniline.

A pale yellow liquid, becoming brownish on keeping, insoluble in water ; b.p.  $195^{\circ}$ .

(1) Dissolve four drops of the base in 6 c.c. of water containing six drops of concentrated hydrochloric acid. Add four drops of a saturated sodium nitrite solution. An oily product (nitrosamine) is obtained. Extract with ether and evaporate the ether. Carry out the Liebermann reaction thus :—Mix together a crystal of phenol and a little of the nitrosamine, heat and add 1 c.c. of concentrated sulphuric acid. An intense green colour is developed which changes to a pale-red on pouring into water. On adding excess of sodium hydroxide solution to the red solution, the colour changes to deep bluish green.

(2) *Acetylation* : (a) *with acetic anhydride*. Cool 1 c.c. of the amine in ice, add 2 c.c. of acetic anhydride a little at a time along with pieces of crushed ice. Stir the mixture repeatedly with a glass rod. Add more ice and continue stirring. The acetyl derivative usually solidifies. If not add solid sodium or ammonium carbonate to neutralise the free acetic acid. The acetyl derivative separates as an oil and solidifies on keeping. Recrystallise from water and determine the melting point. m.p.  $102^{\circ}$ .

(b) *with acetyl chloride*. Dissolve five drops of the amine in 1 c.c. of dry benzene. Add six to eight drops of acetyl chloride, boil gently over a tiny flame till no more fumes are given off. Cool and pour into a watch glass. The benzene evaporates leaving behind the acetyl derivative. Recrystallise from water and determine the melting point.

(3) *Sim n's reactions for secondary amines*. Prepare a fresh solution of acetaldehyde using 2 c.c. of alcohol (1 : 1) exactly as described under formaldehyde with the oxidised copper gauze. To one drop of the secondary amine, add 2 to 3 c.c. of water, 1 drop of 0.5 per cent nitroprusside and 1 c.c. of the aldehyde solu-

tion. A blue coloration which gradually fades to a pale yellow is developed slowly.

(4) *Reaction with benzenesulphonyl chloride.* To eight drops of the amine in a test-tube (6"  $\times$  1") add 8 c.c. of 10 per cent sodium hydroxide and eight drops of the acid chloride. Shake thoroughly and warm gently until the smell of benzenesulphonyl chloride is no longer noticed. Cool, shake well and filter the precipitate. Recrystallise from alcohol and determine the melting point (m.p. 78°).

To a little of the precipitate add sodium hydroxide and note its insolubility. Repeat the experiment using aniline, proceeding exactly as described above. Note the solubility of the sulphonanilide in sodium hydroxide solution.

(5) *Nitration of methylaniline.* Dissolve five drops of the amine in 5 c.c. of concentrated sulphuric acid. Cool in ice water and add ten drops of fuming nitric acid drop by drop with frequent shaking. After two minutes pour slowly into ice water (10 c.c.) and shake vigorously. Collect the precipitate, wash with ice-cold water and recrystallise the tetranitromethyl aniline from boiling alcohol (m.p. 127°C.).

## Tertiary amines

### Dimethylaniline

Colourless liquid when pure but becomes dark on exposure to air, has an odour resembling aniline but less pleasant, is insoluble in water but readily dissolves in dilute acids, b.p. 194°.

(1) Dissolve two drops of the amine in dilute hydrochloric acid and add a solution of potassium ferrocyanide. A white crystalline precipitate of dimethyl-aniline-ferrocyanide is formed. Recrystallise it from hot water.

(2) To four drops of dimethylaniline add twice the amount of methyl iodide and shake. On warming, the quaternary salt is obtained in colourless crystalline plates. Recrystallise from methyl alcohol. (d. 228-229°).

(3) Repeat experiment with benzenesulphonyl chloride exactly as under methyl aniline. No derivative is obtained; hence no reaction takes place.

(4) *Reaction with nitrous acid.* Dissolve five drops of dimethyl aniline in a mixture of 2 c.c. of concentrated hydro-

chloric acid and 3 c.c. of water and cool in ice. Add sodium nitrite drop by drop till there is a slight excess (test with starch iodide paper). Filter off the precipitated p-nitroso-dimethylaniline hydrochloride and wash with 1 c.c. of ice-cold hydrochloric acid. Dissolve the hydrochloride in water in a separating funnel, add a slight excess of sodium carbonate and extract the free base with ether (10 c.c.). Dry the ether extract with potassium carbonate, filter into a crystallising basin and remove the ether by evaporation. p-Nitrosodimethyl-aniline crystallises in grass-green plates (m.p. 85°).

(5) 1-2 drops of the base is heated with a fragment of anhydrous zinc chloride and 3-4 drops of benzaldehyde in a dry test-tube for a minute. The melt is cooled and treated with 3 c.c. of alcohol to which two drops of concentrated hydrochloric acid have been added. An intense green colour is produced (Malachite green).

### Diamines (aromatic)

#### o-Phenylenediamine

A colourless solid easily soluble in hot water, alcohol, chloroform and ether; m.p. 102°.

(1) Dissolve 0.05 g. of substance in 5 c.c. of water to which a few drops of concentrated hydrochloric acid have been added. Add 1 c.c. of a 10 per cent, ferric chloride solution, shake and allow to stand. After a few minutes red needles separate.

(2) (a) Dissolve 0.1 g. of substance in 10 c.c. of alcohol and add a few drops of a hot solution of phenanthra-quinone in acetic acid. A yellow precipitate of 2 : 3 diphenylene quinoxaline is produced. Recrystallise from benzene and find its m.p. (217°).

(b) Repeat the above experiment using an alcoholic solution of the amine and benzil. 2 : 3 Diphenyl quinoxaline is produced. It crystallises from alcohol in colourless needles (m.p. 126°).

(3) Prepare the acetyl derivative as usual taking 0.2 g. of the amine and 12 drops of acetic anhydride. A diacetyl derivative is obtained (m.p. 182-3°).

#### p-Phenylenediamine

A crystalline solid, unstable, slightly soluble in water, best crystallised from benzene, easily soluble in alcohol and ether. m.p. 140°.

(1) Dissolve .05 g. in 10 c.c. water. Add 2 drops of ferric chloride solution. The solution becomes deep green and on further addition of two more drops of ferric chloride, changes to brown and finally becomes violet. An odour of quinone is perceived. This may be confirmed by gently warming the substance with manganese dioxide and sulphuric acid.

(2) To 0.1 g. of substance add 5 c.c. of hydrogen sulphide solution, then 1 c.c. of concentrated hydrochloric acid and lastly a few drops of ferric chloride solution. An intense blue or violet colour is produced.

(3) To 0.1 g. of substance add an equal amount of melted phenol and add sodium hypochlorite solution drop by drop. A violet colour is produced due to the formation of indophenol.

(4) Repeat the above experiment using aniline instead of phenol. A greenish blue colour is formed due to formation of indoamine.

(5) Prepare the diacetyl derivative using 0.1 g. of the base and 8 drops of acetic anhydride. The diacetyl derivative is formed, (m.p. 298-299°).

### **m-Phenylenediamine**

Crystalline solid, slightly soluble in water, very soluble in alcohol and ether, m.p. 63°.

(1) Dissolve .05 g. in 2 c.c. of dilute sulphuric acid, add a dilute solution of sodium nitrite drop by drop. The solution becomes yellow then a brown precipitate of Bismarck brown is obtained.

(2) Repeat experiment (1) as under ortho-phenylenediamine. A red solution is obtained.

### **Nitriles**

#### **Acetonitrile or methyl cyanide**

A liquid with a pleasant smell, miscible with water, b.p. 71°.

(1) Heat a few drops of the nitrile with a dilute solution of sodium hydroxide. Ammonia is evolved.

(2) In a test-tube (6" × 1") fitted with a refluxing arrangement, place 5 c.c. of 50 per cent sulphuric acid and add 3 c.c. of acetonitrile. Boil gently for about 15 minutes. Dilute the contents with 5 c.c. of water and distil collecting about 3-4 c.c. Test the distillate for acetic acid.

Mix the residue with a few c.c. of strong alkali (20 percent) and warm. Ammonia is evolved.

(3) Dissolve a few drops of the nitrile in 1 c.c. of absolute alcohol and add bits of sodium (2 mm.) one after another. Gently warm and test the escaping gas with red litmus paper. Ethyl amine is evolved.

### **Benzonitrile**

A colourless liquid with a strong smell of bitter almonds, insoluble in water, soluble in alcohol, b.p.  $191^{\circ}$ .

(1) Mix 1 c.c. of the nitrile with 5 c.c. of 15-20 per cent. alcoholic potash in a test-tube ( $6'' \times 1''$ ) fitted with a refluxing arrangement. Boil for 15 minutes, test the escaping gas with red litmus paper for ammonia. Evaporate the residue on a water-bath almost to dryness to drive off the alcohol and acidify with dilute hydrochloric acid. Benzoic acid is precipitated. Recrystallise from a little water and find the melting point.

(2) Mix 1 c.c. of benzonitrile with 15 c.c. of hydrogen peroxide (3%) in a beaker. Add a few drops of 2N-NaOH, gently warm the beaker and stir vigorously till the oil disappears. A white precipitate of benzamide is obtained. Filter and crystallise from water or dilute alcohol (m.p.  $126^{\circ}$ ).

(3) To a few drops of the nitrile add a little tin powder and hydrochloric acid (1 : 1) and gently warm for a few minutes. Add strong alkali (15 per cent) till the precipitated hydroxide just dissolves. Benzyl amine is formed which has the strong odour of ammonia.

### **Pyridine**

A colourless liquid with a characteristic unpleasant smell, miscible with water, b.p.  $115^{\circ}$ .

(1) Dissolve 1 c.c. of pyridine in 5 c.c. of water and test with litmus. Note the alkaline reaction.

To 1 c.c. of ferric chloride solution, add 2 c.c. of the aqueous solution of pyridine. Ferric hydroxide is precipitated.

Repeat the experiment with aluminium sulphate. Aluminium hydroxide is precipitated.

The above reactions show the strong basic nature of pyridine.

(2) To 2 c.c. of the aqueous solution, add a drop of dilute hydrochloric acid and then 2 c.c. of a saturated aqueous solution of mercuric chloride. A white crystalline precipitate of the salt  $C_5H_5N.HgCl_2$ , is obtained (m.p.  $177^\circ$ ).

(3) To 0.5 c.c. of pyridine add 5 c.c. of a saturated aqueous solution of picric acid. A crystalline precipitate of the picrate is obtained (m.p.  $167^\circ$ ).

(4) To a few drops of pyridine add 2 c.c. of a dilute solution of permanganate. No decolorisation takes place showing absence of oxidation.

(5) To a few drops of the aqueous solution, add a few drops of dilute hydrochloric acid and then sodium nitrite drop by drop. No particular change beyond decomposition of the nitrite takes place. Hence nitrous acid has no action on pyridine.

(6) To five drops of dry pyridine add an equal amount of methyl iodide. In a few minutes a vigorous reaction takes place and on cooling a crystalline mass of pyridine methiodide is obtained (m.p.  $117^\circ$ ).

(7) Add to a dilute solution of pyridine in water a few drops of Mayer's reagent ; a white precipitate is obtained in plenty which dissolves on heating and crystallises on cooling in long thin prisms.

This is the usual test for an alkaloid which is also answered by pyridine.

### Quinoline

A colourless liquid, with a characteristic bad smell and insoluble in water, b.p.  $238^\circ$ .

(1) Dissolves easily in acids and answers test (1) of pyridine.

(2) Repeat experiment (3) as under pyridine. Quinoline picrate separates in yellow needles. Recrystallise from benzene and find its melting point ( $203^\circ$ ).

(3) Repeat experiment (6) as under pyridine but dissolve the quinoline in a little benzene and boil. The methiodide separates in yellow prisms (m.p.  $73^\circ$ ).

(4) Repeat experiment (7) as under pyridine. The result is quite similar.

(5) To four drops of quinoline add four drops of dilute sulphuric acid and four or five drops of a saturated potassium dichro-

mate solution. A copious precipitate of the quinoline dichromate crystallises in orange yellow prisms (m.p. 164-167°).

(6) To a drop or two of the aqueous solution add a solution of iodine in potassium iodide (1 g. iodine and 1.4 g. potassium iodide in 20 c.c. of water). A reddish brown precipitate insoluble in hydrochloric acid is obtained. This is a very delicate test for quinoline.

### Alkaloids

The term alkaloid is now applied only to the basic substances occurring in plants containing in their constitution nitrogen as part of one or more hetero-cyclic rings. They occur chiefly as salts of organic acids like citric, oxalic, malic etc., in plants. They give precipitates with :

(1) Iodine in potassium iodide—dark yellow or brown precipitates of the periodide.

(2) Picric acid.

(3) Tannic acid.

(4) Phosphotungstic and phosphomolybdic acids.

(5) Mayer's reagent.

These are called alkaloidal reagents and react with bases like aniline and quinoline as well. The particular alkaloid must be ultimately identified by special tests.

### Quinine $C_{20}H_{24}O_2N_2$ .

Sparingly soluble in water, easily in alcohol and other solvents. Crystallises with 3 molecules of water from dilute alcohol (m.p. 176° anhydrous; 57° trihydrate).

(1) Test aqueous solution with litmus. Note the alkalinity.

(2) Dissolve a little quinine in a few drops of chloroform and pour the solution into dilute sulphuric acid. Observe the blue fluorescence. No fluorescence is observed when dilute hydrochloric acid is substituted for oxy-acids.

(3) Dissolve a little quinine sulphate (0.01 g.) in 10 c.c. of water containing a little dilute sulphuric acid (3 drops) add four drops of hypochlorite solution and then ammonia drop by drop. A bright emerald green colour is obtained changing to rose-red on adding a few drops of potassium ferricyanide solution. (This is called the Thalleoquinine reaction.)



*Herepathite test.* 3.2 g. of quinine, 0.5 g. of concentrated sulphuric acid and 0.3 c.c. of distilled water are heated on a water-bath with 20-30 c.c. of absolute alcohol to boiling. While the solution is boiling, 10 c.c. of alcohol containing 1.27 g. of iodine and 0.3 c.c. of hydriodic acid (d, 1.7) are added, and the mixture boiled for a minute. The colour changes from brown to dark green. Cooling yields shining, green crystals of Herepathite which can be recrystallised from boiling alcohol. Yield, 3 g. (m.p. 141°).



### **Strychnine** $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2$ .

Colourless prisms insoluble in water, soluble in alcohol, m.p. 284°. Poisonous.

(1) Moisten a little in a porcelain basin with 1 drop of concentrated sulphuric acid and 1 drop of concentrated nitric acid. Then add a crystal of potassium dichromate and rub with a glass rod. A beautiful blue changing to a violet colour is noticed. The violet colour further changes to red and the solution finally becomes yellow.

(2) To a few drops of the solution of its hydrochloride add ferric chloride solution. A brownish green precipitate is obtained.

(3) Prepare the picrate as usual and find its melting point (275-285°).

### **Nicotine**

Highly poisonous liquid, usually brown in colour, miscible with water, alcohol and ether b.p. 247°.

(1) Repeat experiment (1) as under strychnine. Olive green coloured solution is formed.

(2) Picrate : (m.p. 219°).

### **Nitro-compounds (aliphatic)**

#### **Nitromethane**

Agreeable smell, sparingly soluble in water, soluble in alkalis, b.p. 101°.

(1) Dissolve 0.5 c.c. of nitromethane in 5 c.c. of strong potassium hydroxide, add a few drops of a strong solution of sodium nitrite and then dilute sulphuric acid drop by drop. An intense red colour is produced (salt of nitrolic acid) which disappears on adding excess of acid.

(2) Dissolve a pellet of sodium in absolute alcohol (1 c.c.) and add a few drops of nitromethane dissolved in alcohol. A white precipitate of the sodium iso-nitromethane is obtained. Filter the precipitate, wash with absolute alcohol and dissolve it at once in water and carry out experiment (1).

(3) Add a few drops of nitromethane to a mixture of potassium hydroxide solution and a little zinc dust and gently warm. Test the escaping vapour with red litmus paper and note the alkalinity. At the same time the characteristic fishy odour of methyl amine is perceived.

(4) Dissolve 1 g. of freshly distilled nitromethane and 1.6 g. of benzaldehyde in 6 c.c. of absolute alcohol. Cool the solution in ice and add slowly 1.5 g. of potassium hydroxide dissolved in the minimum amount of methyl alcohol. After a few minutes pour into plenty of water containing dilute hydrochloric acid. The *o*-nitro-styrene which separates out is recrystallised from dilute alcohol (m.p. 58°).

(5) *Reduction to N-methylhydroxylamine.* To four drops of nitromethane dissolved in 2 c.c. of water add 1 g. of ammonium chloride, cool the mixture in ice water and add 1 g. of zinc dust little by little with frequent shaking. Set aside for three or four minutes. Then filter the solution and divide into two parts.

(a) To one part add ammoniacal silver nitrate containing more ammonia than that required just to dissolve the initially precipitated silver hydroxide. A black precipitate of metallic silver is obtained.

(b) To the second part add 1 c.c. of Fehling's solution and warm. Red or orange yellow cuprous oxide is precipitated.

### Nitro-compounds (aromatic)

Mono-nitro compounds are liquids or solids of a yellow colour with a characteristic smell ; insoluble in water.

#### Nitrobenzene

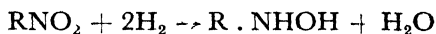
Light yellow liquid with a smell of bitter almonds, sp.gr. 1.208, b.p. 206-207°.

(1) To three drops of nitrobenzene add 1 c.c. of sodium hydroxide and warm. Nitrobenzene does not dissolve as it is not acidic.

(2) Reduce nitrobenzene to aniline as described in Experiment 17 (p.39). Test for the aniline with sodium hypochlorite.

(This test can be made a general one for aromatic nitro-compounds : If the hydrochloride of the primary amine thus produced be diazotised and poured into an alkaline solution of  $\beta$ -naphthol, a red precipitate of benzene-azo- $\beta$ -naphthol is obtained.)

(3) *Mulliken and Barker's reaction.* Dissolve three drops of nitrobenzene in 3 c.c. of alcohol (1 : 1). Add six drops of calcium chloride solution, a pinch of zinc dust, heat to boiling and set aside for five minutes. Cool, filter and to the filtrate add Tollen's reagent. A black deposit of silver is obtained as a result of the formation of phenyl hydroxylamine.



(4) Dissolve three drops of nitrobenzene in 2 c.c. of a mixture of one part of aniline and two parts of p-toluidine. Add 2 c.c. of water, 2 c.c. of concentrated hydrochloric acid, 1 g. of iron filings and heat the mixture. Evaporate almost to dryness in a porcelain basin and pour a little of the dark solution into dilute acetic acid contained in a beaker. A deep magenta colour is produced (para-rosaniline).

(5) To 1 c.c. of nitrobenzene add 4 c.c. of a mixture of equal amounts of concentrated sulphuric and fuming nitric acids and gently heat for about ten minutes. On pouring into water, meta-dinitrobenzene is precipitated. Crystallise from alcohol and determine the melting point ( $90^\circ$ ).

### **m-Dinitrobenzene**

Practically colourless needles, soluble in hot alcohol, m.p.  $90^\circ$ .

(1) Add 1 g. of m-dinitrobenzene to 40 c.c. of boiling water contained in a beaker and then a solution of 1 g. of sodium sulphide and 0.5 g. of sulphur in 8 c.c. of boiling water. Boil the mixed solution for ten minutes and filter hot using a hot water funnel. m-Nitraniline separates on cooling. Recrystallise from boiling water (100 c.c.) and determine its melting point ( $90^\circ$ ).

(2) Add 1 g. zinc dust to a mixture of 0.1 g. of dinitrobenzene, 1 c.c. of water and 2 c.c. of concentrated hydrochloric acid, and warm. After the reaction has subsided proceed exactly as in the reduction of nitrobenzene. Dissolve the m-phenylenediamine in a little water containing a few drops of dilute sulphuric acid and

then add dilute sodium nitrite. A deep brown colour is produced (Bismarck Brown).

### Nitro-phenols

#### **o-Nitro-phenol**

A yellow crystalline substance with a peculiar smell, insoluble in water and volatile in steam, m.p.  $45^{\circ}$ .

(1) To 0.1 g. of the phenol add drop by drop a concentrated solution of potassium carbonate. A dark red crystalline potassium salt is precipitated. Add a few drops of water and heat till a clear solution is obtained. On cooling dark red needles of the salt crystallise.

(2) To a few drops of the alcoholic solution add neutral ferric chloride. No definite colour is noticeable.

(3) Dissolve 0.2 g. of the phenol in dilute caustic soda solution and add solid sodium hydrosulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) little by little to the boiling solution till it is completely decolorised. On filtering and cooling, the amino-phenol crystallises out. Determine the melting point ( $174^{\circ}$ ).

#### **p-Nitro-phenol**

Colourless or pale yellow needles, soluble in water, not volatile in steam, m.p.  $114^{\circ}$ .

(1) Repeat experiment (1) as under o-nitro-phenol. A yellow crystalline precipitate of the potassium salt is obtained.

(2) Same as with o-nitro-phenol.

(3) Repeat as under o-nitro-phenol. The melting point of p-amino-phenol is  $184^{\circ}\text{d}$ .

### Amides

#### **Acetamide**

A white crystalline solid with a peculiar smell, soluble in water, but slightly in ether, m.p.  $82^{\circ}$ .

To 0.5 g. of the amide add 5 c.c. of dilute sodium hydroxide. No smell of ammonia is observed in the cold. Heat the solution to boiling. Note the smell of ammonia. Evaporate the solution to dryness, transfer the solid to a test-tube, add a few drops of concentrated sulphuric acid, and then a few drops of alcohol and warm. Fruity odour of ethyl acetate is formed due to the acetamide being hydrolysed.

(2) Repeat the above experiment using 2 c.c. of dilute sulphuric acid. Cool and add a slight excess of alkali and warm. Ammonia is evolved.

(3) To 2 c.c. of mercuric chloride solution add sodium hydroxide drop by drop till there is a slight excess. Add a little acetamide. The mercuric oxide dissolves to form the soluble mercuric acetamide  $(\text{CH}_3\text{CO NH})_2\text{Hg}$ . On passing  $\text{H}_2\text{S}$  into the solution, mercury is precipitated as the black mercuric sulphide.

(4) To an aqueous solution of acetamide add a few crystals of sodium nitrite and a few drops of dilute sulphuric acid. Acetic acid is formed as a result of the replacement of the  $\text{NH}_2$  group by the hydroxyl group and nitrogen is evolved.

### Benzamide

White crystalline solid soluble in hot water, m.p.  $130^\circ$ .

(1) Treat 0.1 g. of the substance with 3 c.c. of cold dilute sodium hydroxide. Ammonia is not evolved.

(2) Boil a little of the substance with 5 c.c. of strong sodium hydroxide solution (20 per cent.). Ammonia is evolved.

(3) Digest 1 g. of the amide under reflux with 15 c.c. of 15 per cent. NaOH until no more ammonia is evolved. Cool in ice and acidify with concentrated hydrochloric acid drop by drop, (in order to recover the maximum amount of the acid). Benzoic acid is precipitated. Filter and recrystallise from hot water. (m.p.  $122^\circ$ ).

### Urea

White crystalline solid, very soluble in water and ethyl alcohol as well as amyl alcohol but almost insoluble in ether, m.p.  $132^\circ$ .

(1) *Action of heat.* Heat 0.5 g. of the substance in a test-tube above its melting point for about two minutes. Ammonia is given off and at the same time a white sublimate of ammonium cyanate is formed in the cooler parts of the tube. Scrape the sublimate carefully with a thin nickel spatula and moisten a specimen of the solid with a cobalt chloride solution on a watch glass. A blue colour is developed. Dissolve the remainder in 1 c.c. of water, add a tiny crystal of hydroxylamine hydrochloride and then a few drops of neutral ferric chloride. An intense purple colour is developed.

Dissolve the residue (biuret) in 1 c.c. of water and add a drop of a very dilute solution of copper sulphate followed by sodium hy-

dioxide (10 per cent.) added drop by drop. A violet colour is developed.

(2) To 3 c.c. of a strong solution of urea in a test-tube add 1 c.c. of concentrated nitric acid. A white crystalline precipitate of urea-nitrate is obtained (m.p.  $163^{\circ}$ ).

(3) Repeat the above experiment using saturated oxalic acid solution. Urea oxalate is precipitated (m.p.  $171^{\circ}$ ).

(4) Warm a little urea with a solution of caustic soda. Ammonia is evolved. On adding dilute acid to the residual liquid after expelling all the ammonia by boiling, there is a vigorous effervescence due to liberation of carbon dioxide.

(5) In a test-tube with side-tube ( $6'' \times 3''$ ) place 0.2 g. of urea, 0.1 g. of sodium nitrite and 5 c.c. of water. Add 2 c.c. of dilute acetic acid and quickly collect the gas over sodium hydroxide solution in a test-tube. Nitrogen collects in the tube while the carbon dioxide simultaneously liberated is absorbed by sodium hydroxide. Test the gas for nitrogen.

(6) Repeat the above experiment using a solution of urea (0.2 g. in 5 c.c.) and adding alkaline hypobromite prepared by adding 3 drops of liquid bromine to 5 c.c. of 10 per cent. sodium hydroxide solution. Nitrogen is again formed, collected and tested as before.

### Anilides

Colourless solids with no smell, possess definite melting points, insoluble in cold water, but soluble in organic solvents.

### Acetanilide

White rhombic plates, soluble in boiling water, m.p.  $114^{\circ}$ .

(1) Mix 0.5 g. of the substance with 1 g. of dry soda lime and place the mixture in a hard glass test-tube ( $6'' \times 5/8''$ ). Above the mixture place a 2-inch layer of soda-lime and draw out the tube at the mouth so as to form a condenser. Heat the layer of soda lime first and then the mixture. The vapour of the substance is thus made to pass over the soda-lime. Collect the liquid coming over in a test-tube. Oily drops of aniline collect along with a little water. With this carry out—

- (a) reaction with bleaching powder (specific test) ;
- (b) carbylamine reaction ; and
- (c) preparation of tribromaniline.

(2) Boil 0.1 g. of acetanilide with dilute sodium hydroxide and noticed the smell of aniline. Confirm by adding chloroform and heating. Carbylamine is formed.

(3) Introduce 1.0 g. of acetanilide in a test-tube ( $6'' \times 1''$ ) fitted with a reflux arrangement and 6 c.c. of sulphuric acid (1 : 1). Boil for ten minutes. Cool and notice the smell of acetic acid. Distil, collecting the distillate separately and test for acetic acid.

The residual liquid contains the amine as salt. Liberate the free base by adding dilute alkali. Aniline is liberated which may be extracted with ether and tested as in experiment (1).

(4) Dissolve 1 g. of acetanilide in 5 c.c. of glacial acetic acid in a test-tube ( $6'' \times 1''$ ) and add a solution of bromine dissolved in acetic acid (8 drops in 1.5 c.c.) and shake well. After letting the mixture stand for 15 minutes pour into cold water, filter and crystallise the p-bromacetanilide from dilute alcohol (1 : 1). Colourless needles (m.p.  $166^\circ$ ).

### Amino acids

#### Glycine $\text{NH}_2\cdot\text{CH}_2\cdot\text{COOH}$ .

Colourless prisms, soluble in water, slightly in alcohol and ether, sweet taste (m.p.  $232\text{--}236^\circ$ ), chars at  $228^\circ$ .

(1) Dissolve a little in water and test with litmus ; solution is neutral to litmus.

(2) Add a few drops of copper sulphate or acetate to a little of the aqueous solution. A deep blue solution is obtained due to the formation of the copper salt.

(3) Add a drop of ferric chloride to the solution. A deep red colour is formed. On adding a few drops of dilute hydrochloric acid the colour is lost.

(4) To mixture of sodium nitrite and glycine dissolved in water add acetic acid drop by drop. Nitrogen is evolved.

(5) Boil a little of the solution of the acid with sodium hydroxide. No smell of ammonia is perceived.

(6) *Hippuric Acid*. Dissolve 0.75 g. of glycine in 5 c.c. of water, add 1 c.c. of benzoyl chloride and keep the solution alkaline by adding a little sodium hydroxide solution. Shake till the smell of benzoyl chloride has disappeared. Add concentrated hydrochloric acid till the solution is just acid to congo red and set aside for an hour or two. Filter off the crystals and wash with a little ether to

remove the benzoic acid contaminating the hippuric acid formed. Recrystallise from a little hot water (m.p. 187-188°).

**Hippuric acid**  $C_6H_5 \cdot CO \cdot NH \cdot CH_2 \cdot COOH$ .

A white crystalline solid slightly soluble in cold water, easily in hot water and scarcely in ether, m.p. 187-188°.

(1) *Action of heat.* Heat about 1 g. of hippuric acid in a test-tube. The acid melts at first but on continued heating becomes brown with the production of a smell of bitter almonds. A sublimate of benzoic acid is also formed. Scrape the sublimate and add a few drops of sodium carbonate. The sublimate dissolves and on adding hydrochloric acid drop by drop is reprecipitated. Find the melting point of the acid.

(2) Mix a little of the acid with a little soda-lime and heat strongly. Ammonia is given off.

(3) Dissolve a little of the acid in water and add ferric chloride solution. A reddish brown precipitate is formed. On adding dilute hydrochloric acid, the precipitate dissolves and the solution once again deposits crystals of hippuric acid.

(4) Take 1 g. of hippuric acid in a (6" × 1") test-tube, add 15 c.c. of concentrated hydrochloric acid, fit the test-tube with a cork carrying a long tube to serve as condenser and reflux for 15 minutes. Cool and filter off the crystals of benzoic acid. Find the melting point of the acid after recrystallising from a little water. Neutralise filtrate by adding a slight excess of ammonia. Concentrate the solution to half the bulk and add copper sulphate solution to a few c.c. of the solution. A deep blue solution is formed due to copper glyccoll.

### Halogen compounds

These can be classified into three groups :—

(a) compounds derived from the open-chain hydrocarbons by substitution of one or more hydrogen atoms : the alkyl halides, e.g., ethyl bromide, ethyl iodide, chloroform, etc.

(b) compounds derived from the benzenoid hydrocarbons by substitution of the hydrogen (i) in the ring, e.g., chlorobenzene, p-chlorotoluene, etc., and (ii) in the side-chain, e.g., benzyl chloride.

(c) compounds obtained by the replacement of the hydrogen group of acids : the acid halides, e.g., acetyl chloride, benzoyl chloride, etc.



### Alkyl halides

Liquids of low boiling point with a sweet ethereal smell, almost insoluble in water, but readily soluble in alcohol and ether.

#### Ethyl bromide

Colourless liquid, b.p.  $39^{\circ}$ .

(1) Place a few drops of ethyl bromide in a test-tube and add silver nitrate solution and shake. No precipitate is formed in the cold.

To the solution add 1 c.c. of dilute nitric acid and heat. Silver bromide is precipitated on account of hydrolysis.

(2) To four drops of ethyl bromide add 2—3 c.c. of alcoholic silver nitrate. A small amount of silver bromide is formed at first which gradually increases in bulk on shaking.

(3) In a 50 c.c. flask fitted with reflux arrangement place 5 c.c. of ethyl bromide and 20 c.c. of potassium hydroxide solution (2N). Add 2 or 3 pieces of porous porcelain and warm till the layer of ethyl bromide disappears. Distil till half the volume of the liquid has come over. Test the distillate for ethyl alcohol by the iodoform test or by preparing the p-nitro-benzoyl derivative. Neutralise 2 c.c. of the residue in the flask with dilute nitric acid and then add silver nitrate. Silver bromide is precipitated.

(4) Repeat the above experiment using 25 c.c. of 50% alcoholic potash : ethylene is formed. Collect the gas over water by attaching a delivery tube. Note that the gas burns with a luminous flame, and decolorises dilute bromine water when shaken with it.

#### Chloroform

Colourless liquid with a characteristic heavy smell, b.p.  $61^{\circ}$ .

(1) To 1 c.c. of chloroform add a little iodine : a purple solution of the iodine is produced.

(2) Place 1 c.c. of the liquid in a small crucible and try to set fire to it. Note that it does not burn.

(3) Add 2 c.c. of aqueous or alcoholic silver nitrate to a few drops of the liquid. No precipitate of silver chloride is formed.

Repeat the experiment with alcoholic silver nitrate. No reaction is observed even now.

(4) Boil 2 c.c. of chloroform with 10 c.c. of dilute sodium hydroxide for about 15 minutes in a flask fitted with a reflux condenser. Cool and divide the solution into three parts.

(a) To one part add dilute nitric acid in excess and then silver nitrate. Silver chloride is obtained as a white precipitate. The precipitate becomes gradually black due to the formation of metallic silver by the action of the formate produced simultaneously.

(b) Neutralise a second portion with dilute hydrochloric acid and add a few drops of mercuric chloride and heat. Mercurous chloride is precipitated as a result of reduction by the formate formed.

(c) To the third part add Fehling's solution and heat. Cuprous oxide is precipitated.

(5) Warm together a drop of chloroform, a drop of aniline and 1 c.c. of alcoholic potash. Note the formation of phenylcarbylamine recognised by its disagreeable odour.

### Aryl halides

#### Chlorobenzene

A colourless liquid with aromatic odour, insoluble in water b.p.  $132^{\circ}$ .

(1) Place a few drops of the liquid on a piece of copper gauze (vide Beilstein's test for halogens) and introduce into the non-luminous flame of the Bunsen burner. The halogen compound burns with a green-edged sooty flame due to the halogen.

(2) To a few drops of chlorobenzene add 2 c.c. of alcoholic silver nitrate. No reaction takes place showing that the halogen is not displaced.

(3) In a small flask of 50 c.c. capacity fitted with a reflux condenser place 1 c.c. of chlorobenzene and 5 c.c. of sodium hydroxide and add through the condenser 2 c.c. of potassium permanganate (2 per cent.) and boil. No decolorisation of the permanganate takes place.

(4) In a test-tube ( $6'' \times 1''$ ) fitted with refluxing arrangement take 1 c.c. of chlorobenzene, add 5 c.c. of absolute alcohol and then bits of clean sodium till no more are dissolved. Cool and evaporate to drive off the alcohol, add water carefully, then dilute nitric acid and finally silver nitrate. A white precipitate of silver chloride is obtained.

(5) To 1 c.c. of chlorobenzene add a mixture of 4 c.c. concentrated nitric acid and 2 c.c. concentrated sulphuric acid and heat

on a boiling water-bath for about half an hour. Pour into ice cold water and filter the 2 : 4 dinitro-chlorobenzene. Crystallise from alcohol (m.p.  $52^{\circ}$ ).

This shows that the halogenated hydrocarbon resembles in reactivity the parent substance and easily undergoes nitration.

### **Benzyl chloride**

Colourless liquid with an irritating sharp odour (b.p.  $179^{\circ}$ ).

(1) Repeat experiment (2) under chlorobenzene using benzyl chloride. Silver chloride is precipitated gradually showing that it resembles an alkyl halide.

(2) Boil 2 c.c. of the halide with a strong solution of potassium carbonate. Note the disappearance of the irritating odour and formation of a substance with an aromatic odour. Benzyl alcohol is formed. Recover the alcohol by extraction with ether and evaporating off the ether. Test the liquid by a boiling-point determination, or by oxidising to benzoic acid with permanganate.

(3) Boil or reflux a few drops of the halide for half an hour with a strong solution of lead nitrate or cupric nitrate. Note the formation of benzaldehyde.

(4) Oxidise 2 c.c. of the halide in a 100 c.c. round bottom flask fitted with a reflux condenser. Cool and filter off the precipitated manganese dioxide and saturate the filtrate with sulphur dioxide. Benzoic acid is precipitated. Filter and determine its m.p. ( $121^{\circ}$ ).

### **Acid chlorides**

#### **Acetyl chloride**

A colourless liquid with a pungent odour, and fuming in air b.p.  $55^{\circ}$ .

(1) Pour a few drops on a piece of copper gauze and introduce into the flame ; note the incombustibility.

(2) Add drop by drop 0.5 c.c. of acetyl chloride to 2 c.c. of water. The acid chloride is decomposed immediately to form hydrochloric and acetic acids.

(3) Recall here the reaction of alcohol and acetyl chloride.

(4) Recall here the reaction of acetyl chloride and aniline.

### Benzoyl chloride

A colourless liquid with a sharp odour, fuming in air; b.p. 197°.

(1) Repeat experiment (2) as under acetyl chloride. Note that the benzoyl chloride is not decomposed at once. Add 2 c.c. of alkali and gradually heat to boiling. Acidify with dilute sulphuric acid. Benzoic acid is precipitated (m.p. 121°).

(2) Repeat as in experiment (3) under acetyl chloride. Ethyl benzoate is formed.

(3) To 4 c.c. of strong ammonia in a test-tube add  $\frac{1}{2}$  c.c. of benzoyl chloride drop by drop. Cool and filter the benzamide formed. Recrystallise from hot water and find its melting point (130°).

### Sulphur compounds

The more important organic sulphur compounds can be assigned to the following groups :—

- (a) Mercaptans and thiophenols.
- (b) Thioethers.
- (c) Esters of sulphuric acid. Sulphonic acids and their salts.
- (d) Sulphones, sulfoxides.
- (e) Compounds containing nitrogen in addition to sulphur such as the thiocyanates, mustard oils, sulphonamides, etc.

### Mercaptans

These are liquids or solids possessing an unpleasant garlic smell, generally insoluble in water but soluble in alkalis. For the following reactions, ethyl mercaptan (or any other mercaptan) may be used. Ethyl mercaptan boils at 36°.

(1) To 2 c.c. of dilute sodium hydroxide solution (N) add a few drops of the substance. Note that it dissolves readily. Treat a portion of the solution with sodium nitroprusside solution. An intense purple colour is developed.

(2) Using about 1 c.c. of the liquid repeat the reaction with sodium as under alcohol. Note the evolution of hydrogen.

(3) To 5 c.c. of an alcoholic solution of mercuric chloride add 0.5 c.c. of the liquid. The mercury salt is obtained as a white precipitate. Filter and recrystallise from alcohol. Determine the melting point of the mercury salt (76°).

(4) Use lead acetate instead of mercuric chloride. A yellow precipitate of the lead salt is obtained (m.p. 150°).

(5) Dissolve a few drops in alcohol and add a few drops of an alcoholic solution of ferric chloride. A transient blue colour is developed.

(6) Boil 2 c.c. of the liquid with 2-3 c.c. of concentrated nitric acid in a test-tube under reflux. The mercaptan is converted into a sulphonic acid.

**Thiophenol**, b.p. 169°.

Reactions (1) to (4) are quite similar to those with mercaptan.

(5) Repeat reaction (6) as under mercaptan. Convert the sulphonic acid into its sodium salt and prepare the sulphonamide (p.114).

(6) Oxidise 0.5 c.c. with hydrogen peroxide or dilute sodium hydroxide and iodine. Phenyl disulphide is obtained. (m.p.60°)

(7) Benzoyl derivative prepared as with phenol melts at 56°.

### Thioethers

These are for the most part liquids with a disagreeable odour ; insoluble in water but soluble in alcohol and ether.

Use **Diethyl sulphide** ( $C_2H_5$ )<sub>2</sub>S, b.p. 92°.

(1) Carry out reaction (3) as with mercaptan. An addition compound is obtained (m.p. 119°).

(2) Mix 1 c.c. of ethyl iodide with 1 c.c. of the substance and warm, if reaction is slow. Add moist silver oxide and shake well with water and filter. Test a part of the filtrate with litmus. Note the alkalinity. To the rest add a solution of the salt of any of the heavy metals. The metallic oxide or hydroxide is precipitated.

(3) To 1 c.c. of lead acetate solution add sodium hydroxide solution drop by drop till the precipitate of the hydroxide formed just dissolves. Then add an alcoholic solution of the substance. A precipitate of the lead salt is obtained.

### Esters of sulphuric acid

#### Dimethyl sulphate

Colourless liquid, b.p. 188° (poisonous).

(1) Boil 2 g. under reflux with 50 c.c. of water or 15 c.c. of dilute potassium hydroxide solution for about half an hour.

Distil off the methyl alcohol and test for it as usual (p. 53). Acidify the residue with dilute hydrochloric acid and add barium chloride solution. A white precipitate of barium sulphate is obtained.

(2) Prepare  $\beta$ -naphthyl methyl ether ; (p.72).

### Sulphonic acids

The simple sulphonic acids are very deliquescent crystalline solids, highly soluble in water. They are usually encountered in the form of their metallic salts which are also crystalline and easily soluble in water.

Use sodium benzene sulphonate or sodium para-toluene sulphonate.

(1) Ignite a small amount of sodium benzene sulphonate on a porcelain crucible lid. Part of it burns away leaving a residue which is soluble in water and shows an acidic reaction. The residue is sodium hydrogen sulphate. Test for sulphate radical by adding barium chloride and dilute hydrochloric acid.

(2) Melt 1 g. of caustic potash in a small nickel or porcelain crucible and add about 0.5 g. of sodium benzene sulphonate. Keep the mixture in a fused state for five minutes, stirring it occasionally with a stout nickel wire. Cool and dissolve in water and acidify with dilute hydrochloric acid a portion of the solution to liberate the phenol. On adding bromine water drop by drop tri-bromophenol is precipitated.

The phenol can also be converted into its benzoate by dissolving the melt in a little water and treating with benzoyl chloride. The mixture is shaken well and diluted with water. The benzoate crystallises out.

N.B.—This method of identification is particularly useful for phenols which are too difficult to be isolated in a pure state after carrying out the above fusion.

(3) *Preparation of p-toluene sulphonyl chloride.* To 1 g. of sodium para-toluene sulphonate in a dry test-tube add about 1.3 g. of phosphorus pentachloride and heat the mixture on a water-bath with occasional shaking for about half an hour. Cool and add ice-water. Shake at intervals to decompose the phosphorus oxychloride. The sulphonic chloride separates at first as an oil and finally solidifies. Wash the chloride with water, extract with ether, dry over calcium chloride and remove the ether by evaporation.

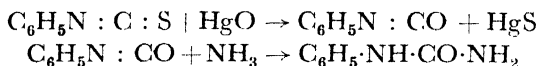
Para-toluene sulphonyl chloride melts at 69°. (Under the same conditions sodium benzene sulphonate gives benzene sulphonyl chloride which separates as an oil and is easily converted into the amide without any purification as described below.)

(4) To about 1 g. of the p-toluene sulphonyl chloride add 5 c.c. of strong ammonia. Shake well until the smell of the chloride has disappeared. Add about 20 c.c. water and evaporate to half the bulk and set the solution aside to crystallise. Filter the crystals and recrystallise from hot water. p-Toluene-sulphonamide melts at 137°.

### Mustard oils

**Phenyl isothiocyanate.** Colourless liquid, insoluble in water with a characteristic penetrating odour, b.p. 221°.

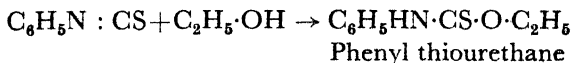
(1) Heat 0.5 c.c. of the substance with 0.5 g. (excess) of mercuric oxide and pass the vapour into a test-tube containing concentrated ammonia. A black precipitate of mercuric sulphide is obtained and at the same time the isocyanate that is formed gives phenyl-urea with ammonia (m.p. 147°).



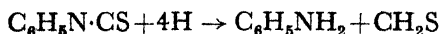
(2) Warm 0.5 c.c. of the substance with 0.5 c.c. of aniline. Thiocarbanilide is obtained. Recrystallise from alcohol and find its m.p. (153°).

(3) Repeat experiment (2) using concentrated ammonia instead of aniline. Phenyl thiourea is obtained (m.p. 154°).

(4) Heat under reflux 2 g. of the oil with 10 c.c. of absolute alcohol in a small round bottom flask till the smell of the oil is no longer perceived. Pour the product into water and recrystallise the solid (phenyl thiourethane) from alcohol. Determine the melting point (84°).



(5) Mix 1 c.c. with 10 c.c. of hydrochloric acid and 2 g. of zinc dust in a flask, and gently heat. An odour of onions due to thioformaldehyde ( $\text{CH}_2\text{S}$ ) is obtained. When the reaction is over, add caustic soda to liberate the aniline. Identify by the usual test.



**Sulphones.** These are stable compounds, unreactive, and unaffected by acids, alkalies, and oxidizing or reducing agents. Aromatic sulphones are nitrated easily while aliphatic sulphones are inert even towards fuming nitric acid.

### Sulphones : Sulphoxides

**Diphenyl sulphone.**  $(C_6H_5)_2SO_2$ . Soluble in benzene, m.p.  $128^\circ$ .

To 3 c.c. of nitrating mixture, add 0.25 g. of the sulphone and warm for a few minutes. The di-m-nitro compound is isolated as usual and crystallised (m.p.  $121^\circ$ ).

**Sulphoxides.** These are readily oxidised to sulphones by nitric acid or finely divided potassium permanganate in glacial acetic acid.

**Phenyl sulphoxide.**  $(C_6H_5)_2SO$ . Easily soluble in alcohol, ether and benzene, m.p.  $70^\circ$ , b.p.  $340^\circ d$ .

(1) Treat a few milligrams with 1 c.c. of concentrated sulphuric acid. A transient blue colour is observed.

(2) Dissolve 0.5 g. in glacial acetic acid and add an excess of a strong solution of permanganate. Pass sulphur dioxide to remove the excess of permanganate and cool in ice. Filter off the precipitated sulphone and recrystallise from absolute alcohol or benzene (m.p.  $128^\circ$ ).

(3) Carry out a reduction with zinc dust in acetic acid. Diphenyl sulphide is formed which can be oxidised as in Expt. (2).



## CHAPTER V

### QUALITATIVE ANALYSIS

Qualitative inorganic analysis aims at the identification of the positive or basic radicals and the negative or acidic radicals present in a given simple substance or a mixture, with the help of the well-known analytical tables. The reactions, being ionic, take place instantaneously in solution. Traces of impurities almost always associated with inorganic salts are very easily detected and seldom offer trouble in the detection of the main constituents. Physical constants, such as the melting point, the boiling point, refractive index, etc., are rarely called into requisition in establishing the identity of an inorganic substance.

In the analysis of organic substances, the purity of a substance is an important consideration, as impurities, if present and not eliminated, are likely to lead to a wrong conclusion as to the identity of a substance. Mere detection of the elements present in a given substance does not give any clue as to the nature or identity of a substance. Reactions, being non-ionic, take place very slowly and largely depend on the manner of combination of the element. Thus chlorine present in the benzene ring, say in *o*-chlorotoluene, differs greatly in reactivity towards alcoholic silver nitrate from that in the side chain as in benzyl chloride. It is on this account that well defined tables of analyses are not possible as in inorganic analysis. Besides, physical constants such as the melting point or the boiling point are of immense importance as confirmatory tests in the case of almost all organic compounds. Nevertheless, it is possible to carry out a rapid analysis of organic compounds by following a methodical procedure without relying too much on the physical constants even at the outset. The procedure may be laid down as follows :

- (1) Establishing the purity of the compound.
- (2) Detection of the elements present.
- (3) Preliminary reactions intended to give general information regarding the nature of the substance.
- (4) Classification reactions which help in assigning the substance to a well defined group or homologous series to which the compound belongs.

(5) Preparation of derivatives and determination of their physical constants with a view to confirm the conclusions reached. This involves a reference to the existing literature about known groups of compounds.

The first step in analysis should be to assign the compound to a particular family or series of which it happens to be a member rather than to establish its identity.

The quantity of the substance given for analysis, usually 3-4 g. should be so portioned out for the various tests, that at least 1 g. could be reserved for preparing a derivative.

**Purity.** The melting point of the substance, if solid, or the boiling point, if liquid, should be carried out with about 0.1 g. of the given substance. A sharp melting point without any previous signs of softening over a long temperature interval shows that the substance is pure. Otherwise it should be crystallised from a suitable solvent. Similarly in the case of a liquid, it should, if pure, distil over an interval of 2-3°. Otherwise the liquid has to be purified by fractional distillation.

**Detection of elements.** The elements that are of common occurrence in organic compounds are carbon, hydrogen, oxygen, nitrogen, the halogens and sulphur, while phosphorus, arsenic, etc. are only very rarely met with. Metals are usually present as salts of organic acids. Carbon and hydrogen are easily tested for by conversion into carbon dioxide and water using cupric oxide as the oxidising agent. There is no direct test for oxygen and the presence of it has to be inferred only by group or classification reactions. Nitrogen, sulphur and halogens are converted by fusing the organic compounds containing these elements with sodium into sodium cyanide, sulphide and halide and the usual inorganic tests are then applied.

In general the elements are usually converted from an organic into an inorganic state of combination before tests are applied, as organic compounds are not appreciably ionised in solution.

**Carbon.** When the substance is known definitely to be an organic compound it is unnecessary to test for carbon. The organic nature of a compound is easily established by igniting a small amount (0.1 g.) of the substance on a platinum foil or on the lid of a porcelain crucible. If the substance burns with a flame or leaves a black residue which gradually burns away leaving no

residue or just a trace of ash, it may be considered as organic. A permanent residue, black or otherwise, which does not disappear even on persistent heating shows the presence of a metal or its oxide.

**Expt.** A small amount of cane sugar is heated on a crucible lid. Inflammable gases are given off while a black residue of carbon is left behind. On heating strongly for sometime, the carbon burns away leaving practically no residue.

The above experiment is repeated using copper acetate. A permanent black residue of cupric oxide is left behind.

**Carbon and hydrogen.** A positive test for carbon and hydrogen is made as follows, only when absolutely necessary. Some pure cupric oxide about 10 g. is ignited in a crucible for about ten minutes to drive away the moisture usually contained

in it. This is allowed to cool in a desiccator and about 0.2 g. of the substance (benzoic acid or acetanilide) is mixed with five times the weight of cupric oxide in a dry mortar and the mixture transferred to a hard glass test-tube ( $5" \times \frac{1}{2}"$ ) fitted with a one-holed cork, carrying a small calcium chloride tube with one bulb (Fig. 36). If the substance is volatile a layer of cupric oxide is placed at the bottom of the tube and another layer of ignited granular cupric oxide

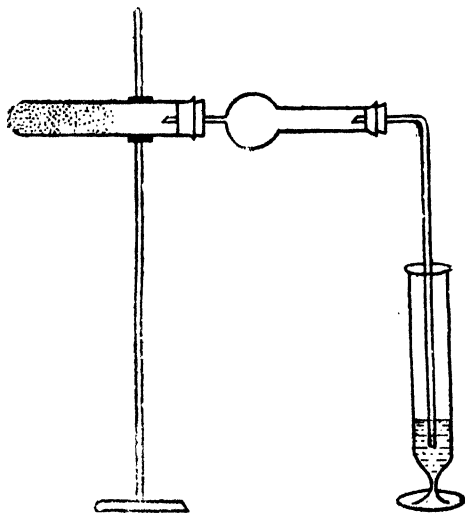


Fig. 36. Apparatus for detecting carbon and hydrogen.

above the mixture. An L tube is attached to the calcium chloride tube and the test tube is clamped horizontally, the L tube dipping into lime-water contained in a test glass. The granular cupric oxide layer is heated first and then gradually the mixture of the substance with fine cupric oxide. The carbon

dioxide formed turns the lime-water milky while drops of liquid collecting in the bulb may be shown to be water by testing with anhydrous copper sulphate which turns blue, thereby proving the existence of carbon and hydrogen in the compound.

**Tests for metals.** The metals and other elements are as a rule tested by the usual methods of inorganic analysis after the organic matter has been destroyed, either by heating to redness on platinum foil or on porcelain in contact with air, or by evaporating to dryness with a mixture of concentrated nitric and sulphuric acids. The latter process is preferable as no charring occurs.

**Tests for nitrogen, halogens and sulphur.** The elements are first brought into inorganic combination by fusing the organic substance with metallic sodium and the products of fusion consisting of sodium sulphide, cyanide, halide or sulphocyanide are then separately tested for.

**Sodium fusion.** A test-tube ( $4" \times \frac{1}{2}"$ ) is suspended on a perforated cemented asbestos plate supported on a ring fixed to a retort stand, so that the tube hangs vertically down (Fig. 37). The test tube is warmed gently; a small piece of sodium, 2 mm. cut from a freshly cleaned piece, is dropped at once after freeing it from the oil adhering to it by means of a filter paper. The tube is heated with a free flame till a layer of sodium vapour purple in colour is formed. The substance, if a solid, is taken on the end of a tiny nickel spatula and dropped directly upon the red-hot bottom of the tube without touching the sides. If the substance is a liquid, three drops of the liquid are sufficient. The flame is removed after a minute or two and when the tube is cold, the lower end, which contained the sodium vapour, is broken by tapping with a pestle into a clean dry mortar. The excess of sodium is decomposed by adding 2 c.c. of alcohol. When the reaction has ceased, the contents of the mortar are ground up with 15 c.c. of distilled water, transferred to a dish, boiled, filtered and the filtrate used for the following tests.

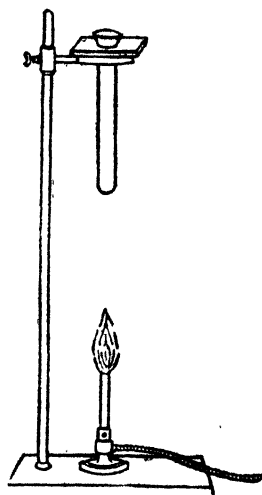


Fig. 37. Lassaigue's test:  
Sodium fusion.

Alternatively, the tube while still hot may be plunged into a porcelain dish containing 10 c.c. of cold water. The glass is shattered and any residual metallic sodium reacts with water. The mixture is stirred, heated to boiling and filtered, the filtrate being usually alkaline. The nitrogen is now present as cyanide, sulphur as sulphide and halogen as halide of sodium.

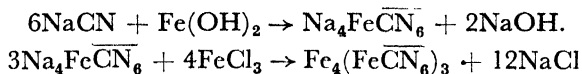
The filtrate is divided into three portions.

**Tests for sulphur.** (1) To 1 c.c. of the alkaline filtrate two or three drops of a freshly prepared solution of sodium nitroprusside are added. A tiny crystal dissolved in 10 c.c. of water will serve the purpose. An intense purple coloration develops and slowly fades away.

(2) To 1 c.c. of the filtrate are added 3 c.c. of alkaline lead acetate solution made by mixing 3 c.c. of bench alkali (2N) with three drops of lead acetate solution. If sulphur is present black lead sulphide is formed. If only a small amount of sulphur is present a yellow colour may be formed without any precipitate. The solution is filtered and the filter paper examined.

(3) *Oxidizing fusion for the detection of sulphur.* A little of the substance, (say 0.05 g.) is mixed with five times the weight of a mixture of 2 parts of sodium carbonate with 1 part of sodium peroxide. The mixture is heated in a nickel crucible gently at first and then strongly till fusion takes place. The melt is cooled, extracted with water, acidified with dilute HCl and the clear filtrate tested with barium chloride. A white precipitate of barium sulphate shows the presence of sulphur.

**Tests for nitrogen. (Lassaigne's).** (1) To 5 c.c. of the alkaline filtrate from sodium fusion, 2 to 3 pea crystals of ferrous sulphate are added, the mixture boiled for a few minutes and filtered. The filtrate contains the ferrocyanide formed and is acidified with a little dilute hydrochloric acid. Another crystal of ferrous sulphate is added and warmed. A blue colour shows the presence of nitrogen. The colour deepens on keeping owing to the oxidation of ferrous sulphate. Excess of ferric sulphate often hinders the formation of prussian blue. When the precipitate is scanty, a turbid greenish colour is imparted to the solution, from which a blue precipitate separates slowly on standing. In such cases, the blue colour may be observed better by filtering. A precipitate or a pronounced blue stain will be left on the filter.



This test is applicable to all nitrogenous compounds excepting diazo compounds which, being unstable, decompose and lose the nitrogen long before the sodium can fix it up as cyanide.

(2) *Modification of Lassaigne's test for nitrogen.* Sometimes volatile nitrogenous compounds, bases or acyl derivatives of bases do not answer the test, the compounds distilling unchanged from the molten sodium.

In such cases, a small quantity of the compound is mixed with five times the weight of a reducing mixture in a crucible which is heated gently at first and then strongly till the reaction is complete. The residue is cooled, boiled with water and filtered. The filtrate contains the cyanide which is tested as before. The reducing mixture is made by mixing 5 g. of potassium carbonate, 4 g. of sodium carbonate and 2 g. of magnesium powder intimately.

(3) *Mulliken and Gabriel's modification.* With explosive compounds (like picric acid, urea nitrate, etc.) a small amount of the compound (say 0.01 g.), is dissolved in a few drops of ether, benzene or alcohol and the solution ground up with ten times the weight of pure naphthalene. The resulting mass is made into pellets. Two or three of these pellets are decomposed with sodium as before and the filtrate treated as under (1). A scanty blue precipitate or a pale bluish stain on the filter paper will usually be seen, if the substance contained even 0.1 mg. of nitrogen.

When nitrogen and sulphur are present together, the filtrate from sodium fusion is acidified with dilute hydrochloric acid till faintly acid and two or three drops of ferric chloride are added. A blood-red colour indicates thiocyanate showing that nitrogen and sulphur are present together. Thiocyanates are generally formed when insufficient sodium is used and the temperature is low.

Sometimes the nitrogen may be missed due to insufficient sodium, as all the sodium combines first with sulphur. It is advisable, therefore, if sulphur is found to be present, to repeat the test using twice as much sodium.

To a portion of the solution add five drops of a freshly prepared ferrous sulphate solution and enough sodium hydroxide to cause a distinct alkalinity. Heat to boiling and filter the precipitated

ferrous sulphide. Acidify the filtrate with dilute hydrochloric acid and then a drop of ferric chloride to obtain the prussian blue.

**Tests for halogens.** (1) *Beilstein's test.* One end of a stout copper wire is coiled round a pencil so as to make a spiral ; the other end is pushed into a cork which serves as a holder. The coil is heated in a flame till it no longer imparts a colour. It is cooled, dipped into the substance and heated again. If a halogen is present, a green colour is imparted to the flame. This test should be repeated a number of times to reach a definite conclusion. It is useless in the presence of free acids and some nitrogen compounds, e.g. urea nitrate, benzamide, acetamide, etc.

(2) If nitrogen and sulphur are absent, 1 c.c. of the filtrate from the sodium fusion is acidified with dilute nitric acid and silver nitrate is added. The colour of the precipitate is an indication of the halogen if only one is present. If the presence of bromine or iodine is suspected, a second portion of the original solution is neutralised with dilute sulphuric acid and 2 c.c. of carbon bisulphide or  $\text{CHCl}_3$  are added. Chlorine water is added drop by drop and shaken. The nature of the halogen can be inferred from the colour imparted to the carbon bisulphide. An iodide may also be tested for, by first acidifying the solution from sodium fusion with dilute sulphuric acid, adding a solution of sodium nitrite and then carbon bisulphide. If a violet solution is produced on shaking, iodine may be inferred.

When nitrogen and sulphur are both present, dilute sulphuric acid is added till faintly acid and the solution is then boiled down to one third of the initial volume. The tests mentioned above are applied afterwards.

(3) *Reduction test for halogens.* A small quantity of the substance is dissolved in absolute alcohol and small pieces of sodium are added one by one, waiting until each piece disappears before adding the next. Thus the halogen is replaced wholly or partly by hydrogen and the halide of sodium is precipitated. A little distilled water is added and the alcohol is boiled off by evaporation nearly to dryness, the residue is acidified with dilute nitric acid and the solution divided into three parts.

To one part chlorine water and carbon bisulphide are added—bromine is indicated if a red solution is obtained, or iodine if the solution is violet.

To the second part bromine water and carbon bisulphide are added—Iodine is detected.

To the third part copper sulphate and ferrous sulphate are added—a white precipitate of cuprous iodide is formed if iodine is present.

(4) *Calcium oxide test.* A small amount of the substance is mixed with halogen-free, freshly heated quicklime, transferred to a hard glass test-tube ( $4'' \times \frac{1}{2}''$ ) and covered with a further layer of lime. Commencing from the upper layer, heating is gradually extended to the mixture and the lower half is raised nearly to redness. The test-tube is then plunged into water, acidified with dilute nitric acid and the halogen tested as before. This method is useful for confirming halogen when associated with nitrogen, as the latter does not interfere.

**Detection of phosphorus.** Phosphorus may be detected by either of the following methods :

(1) A small quantity of the substance is heated with a mixture of concentrated sulphuric and nitric acids until a clear solution is got. The solution is diluted, filtered and boiled with an excess of ammonium nitrate. The solution is cooled, and warmed with ammonium molybdate solution. A yellow precipitate of ammonium phosphomolybdate indicates the presence of phosphorus.

(2) A small amount of the substance is added to a fused mixture of equal parts of potassium carbonate and potassium nitrate in a porcelain crucible and the mixture heated until effervescence ceases. The cooled melt is dissolved in excess of dilute nitric acid and ammonium molybdate is added to the warm solution.

Other elements which occur in organic compounds, such as arsenic, are detected by destroying the organic material by oxidation with concentrated nitric acid in a sealed tube or by fusion with potassium nitrate or sodium peroxide and then applying the usual tests.

A very rough idea of the class to which the compound belongs may thus be obtained when the elements are known.

The types of compounds usually met with are those which contain

1. Carbon and hydrogen
2. Carbon, hydrogen and oxygen



3. Carbon, hydrogen and nitrogen
4. Carbon, hydrogen and halogen
5. Miscellaneous compounds containing carbon, hydrogen, and oxygen with sulphur or nitrogen or halogen.

The following tests are carried out irrespective of the presence of sulphur, nitrogen or halogen.

### Preliminary reactions

#### Physical properties

**Colour.** The coloured compounds that are usually met with in analyses are the nitro and azo-compounds, quinones and some diketones ; they are generally yellow or orange-yellow. Liquid aromatic amines are colourless, when freshly distilled, but become dark on exposure to air due to oxidation.

**Odour.** The characteristic odours can be broadly classified as follows :—

- |                            |     |                                                                         |
|----------------------------|-----|-------------------------------------------------------------------------|
| (a) Spirituous             | ... | Lower aliphatic alcohols (amyl alcohol with characteristic smell).      |
| (b) Light ethereal         | ... | Lower aliphatic ethers.                                                 |
| (c) Heavy ethereal (sweet) |     | Aliphatic halogen-substituted compounds.                                |
| (d) Fruity                 |     | Esters of all kinds.                                                    |
| (e) Ammoniacal or fishy    | ... | Aliphatic amines, the tertiary amines possessing a strong fishy odour.  |
| (f) Aniline-like           | ... | Aromatic amines excepting those with the amino group in the side chain. |
| (g) Phenolic               |     | Aromatic monohydroxy compounds.                                         |

**Solubility behaviour.** It is of great importance to examine the solubility of the substance in various solvents, as it often gives an idea of the chemical nature of a compound. Solubility in water should be tried first and then in alcohol and finally in ether.

Salts of acids and bases are generally soluble in water but not in alcohol or ether.

Acids are soluble in hot water and generally easily in alcohol or ether.

Hydrocarbons are insoluble in water but easily soluble in ether.

Whether a substance is soluble in water or not, its reaction towards litmus should be examined so as to classify it as an acidic, basic or neutral body.

### Chemical tests

**Action of sodium bicarbonate.** Treat 0.05 g. of the substance with 1 or 2 c.c. of strong bicarbonate solution added drop by drop. An effervescence with evolution of carbon dioxide indicates an acidic substance.

Sodium carbonate easily dissolves nitro-phenols and therefore bicarbonate is preferred for this test. Phenols are not affected by this treatment.

**Action of caustic soda.** Treat 0.1 g. of the substance with 2 c.c. of caustic soda solution (10%) and heat, noting the following effects :

(1) Substance unaffected : higher alcohols, ketones, amines, mono-nitro-compounds (aromatic), etc.

(2) Substance affected : oily drops or emulsions formed due to the liberation of amines from amine salts, of chloroform from chloral or chloral hydrate, etc.

(3) Substance dissolves in the cold acids and phenols. Saturate the solution with carbon dioxide. If a precipitate is obtained or an oil is liberated, a phenol is indicated. Poly hydric phenols rapidly become brown due to oxidation.

(4) Change of colour : If the liquid becomes yellow or brown with a peculiar smell, an aliphatic aldehyde or a sugar like glucose, fructose or lactose is indicated.

(5) Evolution of ammonia : (a) in the cold—from ammonium salts ; (b) on heating—from amides or imides.

(6) A strong colour is produced : nitro-phenols or other indicators, if the colour is destroyed by dilute acids.

**Action of dilute hydrochloric acid.** Treat a few drops of the substance, if liquid, or 0.05 g., if solid, with a few drops of dilute acid. If the substance dissolves and is reprecipitated on adding alkali, a substance of a basic nature is indicated.

**Action of concentrated sulphuric acid.** Heat a little of the substance with 1 c.c. of concentrated sulphuric acid in a test-tube and observe the changes :

- |                                                                                                                                                                                                    |                                                                        |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------|
| (1) Substance is immiscible or remains unacted upon.                                                                                                                                               | Aliphatic saturated hydrocarbons are indicated.                        |
| (2) (a) Substance dissolves slowly in the cold without any violent action. The solution, after setting aside for some time and then pouring into ice cold water, liberates the original substance. | An ether.                                                              |
| (b) Reaction same as above but takes place usually on heating. On pouring into cold water, the original substance is not regenerated.                                                              | An aromatic hydrocarbon dissolving slowly by sulphonation.             |
| (3) Chars with smell of burnt sugar.                                                                                                                                                               | Carbohydrates, tartrates, etc.                                         |
| (4) Gases liberated :—carbon monoxide, carbon dioxide, sulphur dioxide.                                                                                                                            | Oxalates, tartrates, etc.                                              |
| (5) Substance mixes and reacts violently.                                                                                                                                                          | Aromatic and aliphatic alcohols ; amyl alcohol gives a red coloration. |

**Reaction with soda lime.** Mix 0.1 g. of the substance with 1 g. of finely ground soda-lime, place the mixture in a hard glass test-tube ( $5'' \times \frac{1}{2}''$ ), nearly fill the test-tube with granular soda-lime and proceed as described on p. 105. Fit with a cork carrying a delivery tube (I tube) dipping in a test-tube containing water. Fix the tube horizontally and heat strongly keeping the soda-lime near the mouth as hot as possible so that any evolved vapours pass over soda-lime. Note the liberation of the following substances :—

- (1) Amines from salts of amines or acyl derivatives.
- (2) Hydrocarbons from aromatic acids.
- (3) Phenols from phenolic acids.

Sulphonates undergo decomposition forming phenols which remain as the phenates ; from these free phenols are liberated by dilute hydrochloric acid.

**Action of bromine in carbon tetrachloride.** Treat some of the substance (0.1 g.) with 1 c.c. of a solution of bromine in carbon tetrachloride in the cold. If decolorisation takes place without evolution of hydrogen bromide, an unsaturated compound is indicated.

If decolorisation takes place with evolution of hydrogen bromide, bromination of a saturated compound is shown.

**Action of bromine water.** Decolorisation shows unsaturation. Formation of precipitates with decolorisation shows bromination having taken place (Cf. tribromo-phenol).

**Action of cold dilute permanganate.** Treat 0.05 g. with 1 c.c. of very dilute permanganate (0.1 per cent). Decolorisation shows unsaturated compounds or easily oxidisable compounds like aldehydes.

**A. Systematic procedure for the analysis of substances containing carbon, and hydrogen with or without oxygen.**

Perform the tests in the following order without omitting any :

(1) **Test for aldehydes.** To 0.05 g. of the substance add 5 c.c. of Fuchsin reagent. Shake well and set aside for two minutes. Do not heat. If a pink, red or blue colour is developed, the substance may be an aldehyde. (When the substance is a solid insoluble in water, dissolve it in the minimum amount of aldehyde-free alcohol.)

Repeat the experiment using Tollen's reagent. If reduction takes place the substance is probably an aldehyde. Polyhydric phenols, amino phenols, etc. answer this test.

(2) **Molisch's test for carbohydrates.** Dissolve 0.05 g. of the substance in 0.5 c.c. of water and add two drops of a ten per cent solution of *L*-naphthol in chloroform. Add carefully 1 c.c. of concentrated sulphuric acid, so that it forms the lower layer without mixing with the rest of the solution. The formation of a red ring at the junction shows the presence of a carbohydrate.

Supplementary tests :—

(a) Test the action towards litmus of **an aqueous** solution of the substance. If the solution is acidic, it is not a carbohydrate.

(b) Note action towards Fehling's solution and toward Barfoed's reagent.

Signs of reduction especially in the latter case show it to be a monosaccharide.

(c) Prepare the osazone using 0.2 g., as described under sugars, and note the time taken for the precipitation of the osazone. Lactosazone is not precipitated from the hot solution. Before drawing any conclusion, cool the solution and see if a precipitate is obtained. If tests (b) and (c) are not answered, the substance is probably a polysaccharide.

(d) Recall the action of concentrated sulphuric acid observed under preliminary reactions. Any colour other than brown or black indicates that the substance is not a carbohydrate.

(e) To 0.05 g. of substance in 1 c.c. of water add one drop of a dilute aqueous solution of ferric chloride. The solution remaining colourless points to the presence of a carbohydrate.

Tests for individual carbohydrates should then be performed on the basis of the evidence obtained from the above experiments.

(3) **Test for acids.** Preliminary reaction with sodium bicarbonate solution should indicate if an acid is present. The following experiment is confirmatory of the acidic nature. Dissolve 0.1 g. of the substance in water or dilute neutral alcohol, add a drop of phenolphthalein and then the bench sodium hydroxide, roughly diluted to N/10, added drop by drop. If the end point is sharp with at least ten drops of alkali having been consumed, the substance may be considered to be an acid.

The identity of the acid should be confirmed by preparing the anilide or the toluidide as described (p. 152).

(4) **Test for esters.** (a) To 0.1 g. of the substance taken in a test-tube (6" × 1") add 2 c.c. of 2N alkali, fit the tube with a one-holed cork and a long glass tube and keep the mixture gently boiling for about half an hour. The disappearance of the oily layer is an indication of the presence of an ester. In the cases of the esters

of benzyl, amyl and isobutyl alcohols, the oily layer will not disappear however long the mixture is boiled. On cooling, the original odour of the ester will have disappeared.

In the case of phenolic esters, the phenol as well as the acid will be dissolved by the alkali. Saturation of the liquid with  $\text{CO}_2$  after saponification precipitates the phenol.

Confirmation of the ester should be obtained by isolating the acid and the alcohol. The distillate contains the alcohol. The residual liquid contains the acid as the sodium salt.

(b) Reflux in a test-tube fitted with a one-holed cork and condensing arrangement 1 c.c. of the ester with 0.25 c.c. to 0.5 c.c. of 2 N methyl alcoholic potash (which keeps indefinitely) and 2 c.c. methanol for 5 minutes. Dilute with its own volume of water after cooling, and add a drop or two of phenolphthalein. There should be no pink colour if the liquid is an ester.

*Treatment of the residual liquid.* Neutralise with concentrated hydrochloric acid, adding the acid drop by drop and note any change.

(a) Insoluble acids like benzoic, salicylic, cinamic, etc., are precipitated at once. Identify as usual.

(b) Moderately soluble acids are not precipitated at once. If the solution is concentrated and cooled, the acids slowly separate out. (Phthalic and succinic acids.)

(c) Soluble acids are tested in the neutralised liquid straight away (acetic, formic, tartaric, oxalic, etc.).

(d) If solid acids are to be isolated, evaporate the solution to dryness, extract with ether three or four times and obtain the acid by evaporation of the ether. A small amount of the acid necessary for a melting point determination can generally be obtained in this way.

(5) **Test for phenols.** To 0.05 g. of the substance dissolved in alcohol or in water add two drops of a dilute, neutral solution of ferric chloride. Formation of a blue, green or violet coloration indicates the presence of a phenol (monohydroxy) or a phenolic compound.

An intense yellow colour shows an  $\alpha$ -hydroxy acid.

Some solid phenols (dihydroxy) do not show this reaction but are soluble in alkali and are precipitated on saturation with carbon

dioxide (see preliminary reactions). Dihydric phenols show reducing properties towards Fehling's solution and ammoniacal silver nitrate. The para compounds are oxidised even by ferric chloride to quinones. Meta-dihydric phenols give the fluorescein test when the para position is free. The ortho dihydric phenols give precipitates with basic lead acetate.

(6) **Tests for carbonyl-group :** (a) When the compound is a solid, take 0.05 g. of the substance in a test-tube fitted with a one-holed cork carrying a long glass tube to serve as a condenser and add 0.5 c.c. of hydroxylamine hydrochloride solution and 2 c.c. of alcoholic sodium hydroxide. Heat in a beaker of boiling water for 10 minutes. Cool, dilute with water and neutralise with dilute acetic acid, cork the tube and shake.

Formation of a precipitate or a turbid solution shows a ketone.

(b) When the compound is a liquid, dissolve two or three drops in water or alcohol (2 c.c.) and add eight drops of the phenyl hydrazine reagent. Shake the tube well and heat for about ten minutes in a beaker containing boiling water. Cool the tube and observe whether a precipitate is obtained or the solution becomes opaque.

(c) The following is usually an unfailing test for carbonyl groups :— Add 0.05 g. of the compound to 2 c.c. of Borsche's reagent, heat to boiling and add 1-2 drops of concentrated hydrochloric acid. At this stage the colour changes generally to yellow or orange. Boil the mixture for a minute, add water to incipient cloudiness and cool. The dinitrophenyl hydrazone crystallises out. In general, the reaction is instantaneous with aromatic ketones and aldehydes and takes a somewhat longer time with the aliphatic compounds. The action is therefore hastened by adding a few drops of water and warming.

(d) When tests *a*, *b* and *c* do not give satisfactory evidence, the preparation of a semicarbazone (p. 65) should be attempted.

Further confirmation of the nature of the compound is obtained by testing with—

(i) Fehling's solution

(ii) Tollen's reagent

(iii) Nitroprusside reagent, following the instructions given under ketones.

(7) **Tests for alcoholic group:** (a) *Action of sodium:* To a few drops of the dry substance contained in dry test-tube add a piece of clean sodium. If the substance is a solid, dissolve 0.05 g. in 1 c.c. of dry benzene and then add the sodium. Heat to  $80^{\circ}$  in a hot water-bath. Rapid evolution of a gas and a change in appearance of the metal indicates the presence of a hydroxylic compound.

N.B. Some esters also react with sodium but they will have been eliminated by this time.

(b) To about 0.1 g. of the substance add 0.4 c.c. of acetic anhydride and heat to  $100-120^{\circ}$  in a glycerine bath for 15 minutes. Then cool and pour into dilute sodium carbonate solution. A fruity odour is noticed if the substance is an alcohol due to the formation of the acetic ester.

The experiment may be repeated using acetyl chloride.

**Type of alcohol.** Whether the alcohol is primary, secondary or tertiary may sometimes be detected by Lucas's test:— To 0.5 c.c. of alcohol in a small test-tube add 3-4 c.c. of the reagent (appendix), keeping the temperature at about  $27^{\circ}$ . The test-tube is corked and shaken. With tertiary alcohols, on account of the rapidity of reaction, the layer of alkyl chloride separates quickly, with secondary alcohols the layer separates in about 5 minutes. Primary alcohols below hexyl do not separate in layers, as they are soluble in the reagent.

The substances that do not respond to the above tests are either ethers or hydrocarbons.

(8) **Ethers.** Ethers are detected by negative tests. They are differentiated from alcohols by tests 7 (a) and (b). The only positive test is the Zeisel test.

To 0.5 c.c. of the substance, if liquid, or 0.5 g., if solid, dissolved in dry carbon-bisulphide or benzene in a test-tube ( $6" \times 1"$ ) fitted as shown (Fig. 38), add 5 c.c. of hydriodic acid (sp. gr 1.7). Attach a test-tube containing a few drops of dimethylaniline to the long refluxing tube. Place the test-tube in a glycerine bath heated

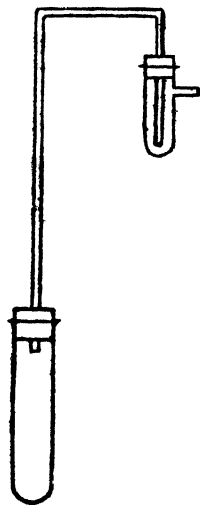


Fig. 38. Apparatus for decomposing an ether.



to 100°-130°, while a current of dry  $\text{CO}_2$  is bubbling through. The dimethylaniline is converted into the quaternary salt which is precipitated, while the phenol liberated remains in the tube. Add a little ether, filter off the crystalline precipitate of quaternary salt, wash with dry ether and determine its melting point. From the melting point, the nature of the alkyl group can be inferred.

Treat the residual liquid in the test-tube with sodium-bisulphite till it is decolorised. Extract with ether twice and shake up the ethereal solution with sodium hydroxide to remove the phenol formed; add benzoyl chloride to the alkaline solution and shake, keeping the liquid alkaline. The benzoyl derivative of the phenol is precipitated. Filter, recrystallise from alcohol and determine its melting point.

(9) **Hydrocarbons.** A substance not responding to any of the tests mentioned above must of necessity be a hydrocarbon. Confirmatory tests are carried out as described under hydrocarbons (preparation of a nitro-derivative or a picrate). From the melting points of the derivatives, the nature of the hydrocarbon is inferred.

**B. Systematic procedure for the analysis of substances containing carbon, hydrogen and nitrogen (a) without oxygen and (b) with oxygen.**

From the preliminary reactions outlined already, namely, (1) colour, (2) action towards cold dilute sodium hydroxide or hydrochloric acid, (3) action towards strong sodium hydroxide solution both hot as well as cold, etc., a general idea of the nature of the substance can be obtained. Excepting the nitro- and the azo-compounds most of the nitrogen compounds are practically colourless. Nitrophenols dissolve in sodium hydroxide to form coloured solutions, while amides and ammonium salts of acids give ammonia with sodium hydroxide. Substances with aniline-like odour or ammoniacal odour are easily distinguished as aromatic and aliphatic amines respectively.

**(a) Without oxygen**

1. **Amines.** Carry out the reactions in the following order:—

(1) Ammoniacal and fishy odour, gaseous and easily inflammable, indicates aliphatic nature.

(2) Solubility and alkalinity. Easily soluble in water forming strongly alkaline solutions which precipitate the hydroxides of metals, indicates aliphatic amines.

(3) *Tests for primary amines :*(i) *aliphatic*

(a) Carbylamine reaction ; (b) Action of nitrous acid ; brisk nitrogen evolution and formation of alcohol ; (c) Rimini's test (p. 90).

(ii) *Aromatic*

(a) Carbylamine reaction ; (b) Action of nitrous acid : the diazo reaction with formation of phenol and coupling diazo-compound with  $\beta$ -naphthol to form an azo-dye ; (c) Acetylation with acetyl chloride or anhydride.

(4) *Secondary amines.* (a) Reaction with nitrous acid with formation of nitrosamines, and application of Liebermann's test ; (b) Simon's reaction (p. 93) ; (c) Formation of acetyl derivative.

(5) *Tertiary amines.* (a) Reaction with nitrous acid : aliphatic amines do not react, while alkyl anilines react with formation of *p*-nitroso-compounds when the para position is free. These nitroso-compounds do not show the Liebermann's test ; (b) Reaction with methyl iodide with formation of quaternary compounds ; (c) Action of acetic anhydride : No reaction.

2. **Nitriles.** These are insoluble both in alkali and acid and the aromatic nitriles possess an odour recalling that of benzaldehyde. Carry out the hydrolysis using 1 g. of substance and 20 c.c. of hydrochloric acid (2 : 1) or sulphuric acid (50%) and identify the acid as previously described (p. 96).

(b) **With oxygen**

These compounds can be classified into the following groups :—

I. Nitro-compounds : Nitro-hydrocarbons, (aliphatic and aromatic), Nitrophenols, etc. ; II. Amides, Imides and Anilides ; III. Amino-acids and IV. Ammonium salts of acids.

1. **Nitro compounds.** Tests for nitro-groups :—(a) *Mulliken and Barker's reaction.* Carry out the reaction with 0.1 g. of the substance as described (p. 102) ; (b) Reduce a little of the substance with tin and hydrochloric acid. Divide the solution into two parts. To one part add excess of sodium hydroxide. A smell of ammonia or a fishy odour indicates an aliphatic nitro-compound. With the remainder carry out test (3) (ii). (b) under aromatic primary amines. The production of a highly coloured precipitate or solution shows the presence of an aromatic nitro-compound.

**Amides, imides, anilides.** (a) Hot strong sodium

hydroxide or distillation with soda-lime liberates ammonia in the case of amides and imides while the base itself is liberated in the case of anilides and toluidides. (b) Carry out a hydrolysis with hydrochloric acid (2 : 1) of 1-2 g. of the substance for 1 hour under reflux. On cooling, the acid if insoluble is precipitated, and can be identified. If soluble, the acid is obtained by distillation, while the base is left in the residue as hydrochloride. The base is liberated by alkali, extracted with ether and identified in the usual way.

(N.B. Anilides and toluidides usually give the carbylamine reaction owing to slight hydrolysis with alkali.)

3. **Amino acids.** Try (a) solubility in water and action towards litmus ; (b) action of sodium carbonate and dilute hydrochloric acid ; (c) action of copper acetate or copper sulphate : formation of deep blue solutions of the respective copper salts ; (d) soda lime distillation which generally liberates the amine ; (e) action of nitrous acid : the amino group is replaced by hydroxyl the presence of which is tested with ferric chloride whereby a purple colour is produced in the case of aromatic acids when the hydroxyl group is in the ortho-position and a yellow colour in the case of aliphatic acids when it is in the  $\alpha$ -position.

4. **Ammonium salts.** (a) are very soluble in water ; (b) with dilute sodium hydroxide ammonia is liberated even in the cold ; (c) when treated with dilute mineral acids, the organic acid is precipitated, if insoluble.

**C. Systematic procedure for the analysis of substances containing carbon, hydrogen and halogen (a) without oxygen and (b) with oxygen.**

(a) **Without oxygen.**

These are mono- or poly-halogen derivatives of the paraffins or aromatic hydrocarbons.

The following general tests are carried out :—(i) *Odour* : sweetish ; halogen-substituted aliphatic hydrocarbons ; pungent : aromatic compounds with halogen in the side-chain ; (ii) *Action of sodium hydroxide* (vide preliminary reactions) ; (iii) *Flame test* to show richness of carbon ; (iv) *Action of alcoholic silver nitrate* to show whether the halogen is in the side-chain or in the ring in the case of aromatic hydrocarbons ; (v) *Confirmatory tests through the preparation of derivatives.*

**(b) With oxygen.**

These are sub-divided into (1) acid chlorides, (2) halogen-substituted acids and (3) others including halogen-substituted phenols, alcohols, ethers, ketones, aldehydes, etc.

(1) **Acid chlorides.** (i) *Odour* : pungent smell and fuming in air. (ii) *Action of water.* Add water drop by drop to a little of the substance ; decomposition takes place with formation of the hydrogen halide and the respective acid. Add silver nitrate ; the silver halide is precipitated. (Aromatic acid chlorides decompose only slowly in the cold but more quickly on heating.) (iii) *Action of sodium hydroxide.* Repeat experiment (ii) using dilute sodium hydroxide. The sodium halide and the sodium salt of the acid are formed. Acidify with dilute nitric acid : the acid if insoluble is thrown down. Add silver nitrate to the filtrate : the silver halide is precipitated. (iv) *Action of strong ammonia or aniline* ; on shaking a vigorous reaction takes place and the amide or the anilide of the acid is precipitated.

(2) **Halogen-substituted acids.** These are strongly acidic, corrosive solids which do not fume in air.

•(a) *Action of sodium hydroxide.* Aromatic acids dissolve without the halogen being replaced. On acidifying, the original acid is precipitated.

Aliphatic acids have their halogen replaced by the hydroxyl group on gently boiling with dilute sodium hydroxide ; thus, monochloroacetic acid gives glycollic acid, trichloroacetic acid gives chloroform and sodium carbonate, and so on.

(b) *Sodalime reaction* : Carry out the test as described before, passing the product into water. Halogen-substituted hydrocarbons are obtained and are tested for as usual.

**D. Systematic analysis of substances containing carbon, hydrogen and sulphur (a) with oxygen or nitrogen or with both, (b) with oxygen and halogen and (c) without any other element.**

These compounds may be referred to the following types :—  
 (i) Sulphonic acids or their metallic salts. The free acids are somewhat rare. (ii) Thio-ureas and substituted thio-ureas. (iii) Mustard oils. (iv) Sulphonamides. (v) Sulphonyl chlorides. (vi) Mercaptans and thio-ethers.

By carrying out the following tests the nature of the compound can be readily inferred :—

<i>Test</i>	<i>Observation</i>	<i>Inference</i>
(a) Odour.	Pungent without fuming in air. Pungent with fuming in air. Very disagreeable garlic like smell.	Mustard oil. Sulphonic chlorides. Mercaptans and thioethers.
(b) Solubility in water.	Readily soluble with strong acid reaction. Very sparingly soluble and showing acidic reaction only after boiling with water.	Free sulphonic acids. Sulphonic chlorides.
(c) Action of alcoholic sodium hydroxide.	Evolution of ammonia Liberation of amines	Sulphonamides and thioureas. Substituted thioureas.
(d) Action of concentrated hydrochloric acid.	Liberation of mustard oils.	Substituted thioureas, <i>e.g.</i> , Thiocarbamide.
(e) Fusion with alkali and treating the melt with dilute acid after dissolving in water.	(i) Evolution of hydrogen sulphide.	Thiourea. Thiocyanates.
	(ii) Evolution of sulphur dioxide and formation of phenol as revealed by test with ferric chloride.	Sulphonic acids or their metallic salts.
	(iii) Evolution of sulphur dioxide and precipitation of silver chloride when treated with silver nitrate in dilute nitric acid.	Sulphonic chlorides.
	(iv) No phenol is formed but barium sulphate is precipitated when treated with barium chloride.	Amino sulphonic acids.
	(v) No phenol is formed but ammonia is evolved during fusion and sulphur dioxide is liberated on acidifying.	Sulphonamides.

Sulphoxides and sulphones are feebly reacting substances and are identified by an elimination process and by the tests given on p. 115.

## CHAPTER VI

### PREPARATION OF DERIVATIVES

The final stage in the analysis of a simple organic substance is the preparation of a suitable derivative, the physical and chemical properties of which furnish confirmatory evidence of the identity of a compound whose relation to a particular class has been deduced by classification reactions. Where a number of derivatives is possible with a given substance, the choice of a derivative should be based on the following considerations.

(1) The derivative should preferably be a solid, because of the ease of manipulation in the matter of preparation and purification, especially when small quantities are dealt with.

(2) The derivative should possess such physical and chemical properties as will enable an absolute differentiation being made between several possibilities.

(3) The derivative should lend itself to preparation by a simple and general reaction which gives a good yield of a fairly pure product. When traces of isomeric compounds are inevitably formed such as the ortho-compound when the para- is required, the required compound should be capable of easy separation and purification.

(4) The derivative should be capable of being prepared with the chemicals ordinarily available in the laboratory and in a moderately short time.

(5) A solid derivative should as far as possible melt at a different temperature from the original solid substance. If that is not the case, the derivative should be distinguished from the original by a mixed melting point test or by a simple solubility test.

At least two derivatives should ordinarily be prepared.

In the cases of some substances, derivatives are often obtained while carrying out the classification reactions, which may serve for use in the final identification.

#### **Types of derivatives commonly used in the identification of the different classes of compounds.**

##### **Hydrocarbons**

The main reactions used in connection with the identification of aromatic hydrocarbons are (a) nitration, (b) oxidation of side-

chains, (c) *sulphonation*, which is only *rarely carried out*, the resulting sulphonic acid or its salt being converted into sulphonic chloride and thence into the amide; (d) preparation of the *picrates*, especially in the case of hydrocarbons of the condensed type (naphthalene, anthracene, etc.).

**Nitration.** (a) When a mono-nitro derivative is required 0.25 g. of the hydrocarbon is added slowly to a mixture of 1 c.c. concentrated nitric acid and 1 c.c. concentrated sulphuric acid, shaking thoroughly after each addition. The mixture is gently warmed for a minute by immersion in a hot water-bath maintained at 60-70°. After cooling, the reaction mixture is poured into a little ice water. The nitro-compound usually separates as an oil and may be purified by distillation or crystallisation from alcohol, if a solid.

N.B.—The oily substance may often be a mixture of two isomers.

(b) *Polynitro derivatives.* To 1 c.c. of fuming nitric acid, 1 c.c. of 5% fuming sulphuric acid or ordinary concentrated sulphuric acid is added and then 0.2 g. of the hydrocarbon. The mixture is warmed on the boiling water-bath for 2 to 3 minutes, cooled and the product isolated as described above.

**Oxidation of the side-chain.** 1 c.c. of the hydrocarbon is oxidised as described (p. 52). The process requires half to three quarters of an hour on the average, and it is advisable to concentrate the filtrate to about a third of the bulk before acidifying or saturating with sulphur dioxide. If the acid has a high melting point (above 300°), a solid ester may be prepared and its melting point determined, *e.g.*, in the case of terephthalic and isophthalic acids which are identified by their methyl esters. (See p. 155).

**Sulphonation.** Although sulphonation is an important classification reaction and serves to distinguish the saturated aliphatic from the aromatic hydrocarbons, it is seldom used for purposes of identification, as the sulphonic acids or their salts are soluble in water and hence difficult to isolate. The sodium salts which are commonly prepared are *dried first* and then converted into the sulphonic chlorides from which the sulphonamides are prepared. The latter crystallise well and have definite melting points. The most satisfactory sulphonating agent is fuming sulphuric acid containing 15-20% of the anhydride. The generation of heat and the slow but complete solution of the hydrocarbon in

the acid without charring indicates that reaction has been completed.

Sulphonation proceeds more readily with the higher homologues of benzene, than with benzene itself ; thus o- and m-xylene are sulphonated readily even by the ordinary concentrated acid.

**Procedure :** To 0.5 c.c. of the hydrocarbon are added 1.5 c.c. of 20% fuming sulphuric acid in a test-tube ( $6'' \times \frac{5}{8}''$ ) and the mixture shaken at first gently and then more vigorously. The mixture is set aside for 5 minutes for the reaction to be completed and then poured into 10 c.c. of ice-water and filtered. The filtrate is saturated with sodium chloride (2-3 g.). If the sodium salt of the sulphonic acid does not separate at once, the mixture is cooled in ice for sometime and the sodium salt filtered, washed with very little ice-water and dried in an air-oven.

The dry salt is gently warmed with a slight excess of phosphorus pentachloride. There is usually a vigorous reaction with evolution of hydrogen chloride, and when the reaction has subsided, the product is treated with a little ice-water and finally evaporated with concentrated ammonia or solid ammonium carbonate in a dish. The sulphonamide crystallises from hot water or dilute alcohol.

**Picrates.** These are usually prepared either in benzene or in alcoholic solutions according to the directions given in the case of the preparation of naphthalene picrate. (p. 52).

General instructions for the preparation of derivatives of the commoner hydrocarbons are given below.

**Ethyl benzene,** b.p.  $136^{\circ}$

(1) *Benzoic acid* : Oxidation of side-chain as described (p. 52). The oxidation is slow and the yield poor.

(2) *p-Sulphonamide* : Prepared as described under o-xylene. (m.p.  $109^{\circ}$ ).

**p-Xylene,** b.p.  $138^{\circ}$

2 : 3 : 6-*Trinitro derivative*. To a mixture of 2 c.c. of concentrated sulphuric acid and 1 c.c. of fuming nitric acid add 5 drops of the compound. Boil gently for a minute over a small flame. Pour into ice-water and crystallise the solid from rectified spirits, (m.p.  $137^{\circ}$ ).

**m-Xylene,** b.p.  $139^{\circ}$

(1) 2 : 4 : 6-*Trinitro derivative*. (m.p.  $180^{\circ}$ ). Preparation as described above.



(2) *Isophthalic acid*. Oxidation of side-chain. (See p. 52).

**o-Xylene**, b.p. 142°

(1) *o-Xylene-sulphonamide*. Sulphonate 0.5 c.c. of the hydrocarbon as described (p. 139) and dry the sodium salt in an air-oven. To 0.5 g. of the salt add about 1.5 g. of phosphorus pentachloride and heat gently for 10 minutes. Cool and pour into ice-water, wash the precipitate with cold water by decantation and boil the sulphonic chloride with 3 c.c. of concentrated ammonia, till the smell of ammonia has disappeared. Dilute with water and boil. Cool in ice and filter the crystals of the sulphonamide (m.p. 144°).

(2) *Phthalic acid*. Carry out the oxidation (p. 52) and perform the fluorescein test.

**Mesitylene**, b.p. 164°.  $C_6H_3(CH_3)_3$  1 : 3 : 5.

2 : 4 : 6-*Trinitro derivative*. Preparation is the same as in the case of trinitro-p-xylene. Colourless needles from alcohol, (m.p. 235°).

**Pseudocumene**, b.p. 168°.  $C_2H_5(CH_2)_4$  1 : 2 : 4.

3 : 5 : 6-*Trinitro derivative*. Preparation as with p-xylene, (m.p. 185°).

**p-Cymene**, b.p. 175°.

(1) *Terephthalic acid*. Oxidise as described (p. 52). Sublimes at 300°. Prepare the methyl ester (m.p. 140°) of the acid (*vide* reactions).

(2) *Sulphonamide*. Preparation similar to o-xylene sulphonamide, (m.p. 115°).

**Phenanthrene**, m.p. 100°

*Picrate* (from alcoholic solution). Long orange-yellow needles, (m.p. 143°).

### Derivatives for alcohols

(1) Preparation of solid esters, chiefly

(a) 3 : 5-Dinitro-benzoates

(b) Benzoates

(c) Acetates.

(2) Oxidation products.

(3) Urethanes.

(4) 3-Nitrophthalates.

## 1. Preparation of solid esters

Water soluble alcohols which are likely to contain moisture are best characterised by the preparation of their 3 : 5-dinitrobenzoates.

(a) *3 : 5-Dinitrobenzoates.* (i) 1 c.c. of the alcohol is mixed with a solution of 1 g. of 3 : 5-dinitrobenzoyl chloride in 10 c.c. benzene and 5 c.c. pyridine are added. After keeping at room temperature for three hours, (tertiary alcohols require additional heating at the boiling point for 30 minutes), the mixture is placed in separatory funnel, diluted with dry ether, washed successively with dilute hydrochloric acid, dilute sodium hydroxide and a large volume of water. The ester is isolated by removal of ether and drying the residue in a desiccator. Recrystallisation is effected from benzene or petroleum ether.

(ii) When the alcohol is present in aqueous solution in low concentration, the following procedure may be adopted. 0.5 g. of crystalline sodium acetate and 10 c.c. of a 40% aqueous solution of sodium hydroxide are added to the alcohol. 5 c.c. of a solution of 3 : 5-dinitrobenzoyl chloride prepared as below, is added after shaking and cooling in ice alternately during 30 minutes. The liquid is extracted with ether, the ethereal layer washed successively with an equal volume of water, dilute hydrochloric acid (5%) and then water and the solvent removed. The residue is recrystallised from petroleum ether or alcohol.

*Preparation of 3 : 5-dinitrobenzoyl chloride solution :* 25 g. of 3:5-dinitrobenzoyl chloride is dissolved in dry petroleum ether (50 c.c., b.p. 80-120°), washed with concentrated sulphuric acid and diluted with 250 c.c. dry benzene.

(b) *Benzoates.* The benzoates are prepared by the Schotten Baumann reaction (p. 66). The monohydric alcohols usually give liquid esters, while solid esters are obtained from polyhydric alcohols such as glycerol, and ethylene glycol.

(c) *Acetates.* Solid acetates are usually obtained in the case of sugars and other polyhydroxy compounds.

## 2. Oxidation products

Oxidation is carried out by (a) chromic acid mixture and (b) alkaline permanganate.

The oxidation results in the formation of volatile aldehydes from primary alcohols and volatile ketones from secondary alcohols.

The products are distilled over and derivatives of the oxidation products are prepared.

**Expt.** (a) *Oxidation with chromic acid mixture.* In a 25 c.c. distilling flask 9-10 drops of the chromic acid mixture are placed along with 10 c.c. of water and 0.5 c.c. of the alcohol added drop by drop while cooling. The flask is closed with a cork. The side-tube is connected to a bent-tube dipping into a test-tube with a side-tube containing 1 c.c. of water (Fig. 26a) and is surrounded by ice water. The contents of the flask are heated till half of the liquid has distilled over. The distillate is converted into a suitable derivative (p. 144).

(b) *Oxidation with alkaline permanganate.* This procedure is particularly useful for aromatic alcohols with a  $\text{CH}_2\text{OH}$  group, e.g., benzyl alcohol, anisyl alcohol, etc. The oxidation is carried out as described under hydrocarbons and the insoluble acid isolated. Oxidation takes place much more readily than with the hydrocarbons.

### 3. Urethanes

The most general derivatives of primary and secondary alcohols are the  $\alpha$ -naphthyl-, *p*-nitrophenyl- and phenylurethanes. These are formed when the alcohol is treated with  $\alpha$ -naphthyl-, *p*-nitrophenyl-, and phenyl isocyanate respectively.

The presence of water as an impurity in the alcohol causes some difficulty in obtaining pure urethanes. Water hydrolyses the isocyanates to give arylamines which combine with the excess reagent to give disubstituted ureas. The ureas are higher melting and less soluble than the urethanes. The procedure is most useful for alcohols insoluble in water and hence obtained easily in anhydrous condition. Tertiary alcohols react with isocyanates only with great difficulty. The isocyanates cause dehydration to occur with formation of the olefine and diaryl urea.

1 g. of the anhydrous alcohol is placed in a test-tube and 0.5 g. of phenyl isocyanate or  $\alpha$ -naphthyl isocyanate added. If a spontaneous reaction does not take place, the tube is warmed on a steam-bath for 5 minutes. It is then cooled in ice and crystallisation is induced by scratching with a glass rod. The derivative is purified by recrystallisation from petroleum ether or carbon tetrachloride. The same procedure can be applied also to phenols.

#### 4. 3-Nitrophthalates

The 3-nitrophthalates are valuable derivatives for the characterisation of alcohols. A mixture of 3 g. of 3-nitrophthalic anhydride and a lower aliphatic alcohol about 2.5 g. is heated in a water bath under reflux for one to two hours. After cooling, the solid is collected by filtration, washed with cold water and recrystallised from water.

With the higher alcohols, a mixture of the anhydride (3 g.) and the alcohol (1 g.) dissolved in pure dry toluene is heated under reflux for 3 hours. The solvent is removed and the residue purified by recrystallisation from aqueous alcohol (30 to 40%).

**Isopropyl alcohol**, b.p. 83°.

Miscible with water, gives iodoform reaction immediately on mixing the reagents.

(1) *Acetone*. Oxidation with chromic acid is carried out as described (p. 142). Acetone is obtained from which (a) dibenzylidene acetone, or (b) 2 : 4-dinitrophenylhydrazone of acetone is prepared.

(2) 3 : 5-dinitrobenzoate, (m.p. 122°).

**n-Propyl alcohol**, b.p. 97°.

Miscible with water ; does not give iodoform reaction.

(1) 0.5 c.c. of the alcohol is oxidised using 0.75 c.c. of chromic acid mixture and the resulting aldehyde passed into a test-tube containing 0.3 g. of  $\beta$ -naphthol dissolved in a mixture of 3 c.c. of glacial acetic acid and a few drops of concentrated hydrochloric acid. The mixture is boiled gently for a few minutes ; water is added drop by drop till a precipitate is formed. This is filtered and recrystallised from dilute alcohol. Colourless plates of propylene-di- $\beta$ -naphthol are obtained (m.p. 153°).

(2) 3 : 5-dinitrobenzoate, (m.p. 74°).

**Ethylene glycol**, b.p. 198°.

Viscous, soluble in water. Heated with solid potassium hydrogen sulphate gives acetaldehyde.

**Ethylene glycol dibenzoate**. Using three drops of alcohol, benzoylation is carried out as described under glycerol (p. 57) and the product crystallised from dilute alcohol, (1 : 1) (m.p. 71°).

#### Derivatives for aldehydes and ketones

The derivatives usually prepared for the characterisation of aldehydes and ketones are

- (1) Phenylhydrazones
- (2) Substituted phenylhydrazones like *p*-nitro- and 2 : 4-dinitrophenylhydrazones
- (3) Semicarbazones
- (4) Oximes
- (5) Oxidation products, chiefly for aldehydes
- (6) Dimedone derivatives, specific for aldehydes.

### 1. Phenylhydrazones

Phenylhydrazones of the lower aldehydes such as formaldehyde and acetaldehyde and of ketones like acetone and methyl ethyl ketone are usually liquids. Aromatic aldehydes and ketones give on the other hand solid derivatives, the time of reaction varying with the nature of the substance.

*Preparation of phenylhydrazones.* A solution of phenylhydrazine is prepared by dissolving 1 g. of the hydrochloride and 1.5 g. of sodium acetate in 10 c.c. of water. The aldehyde or ketone (0.5 g.) is dissolved in a little alcohol and added to the phenylhydrazine solution, more alcohol being added if necessary to give a clear solution. The mixture is heated on a steam bath for about 30 minutes. The phenylhydrazones often separate first as oils on cooling. Purification is effected by recrystallisation from alcohol.

### 2. Preparation of *p*-nitro and 2 : 4-dinitrophenylhydrazones

*p*-Nitrophenylhydrazine and 2 : 4-dinitrophenylhydrazine form well-defined, easily-isolable derivatives with aliphatic aldehydes and ketones.

A mixture of 1.5 g. of 2-4-dinitrophenylhydrazine, 2 c.c. of the aldehyde or ketone and 100 c.c. of 95% alcohol is brought to boiling. The flame is removed and 2 c.c. of concentrated hydrochloric acid is added. The colour usually changes and the solution becomes clear. The mixture is then boiled under reflux for ten minutes and is allowed to cool to room temperature. The product is removed by filtration, washed with a little cold alcohol and recrystallised from alcohol, ethylacetate or chloroform.

### 3. Semicarbazones

(a) *For water soluble compounds.* 1 c.c. of the aldehyde or ketone, 1 g. of semicarbazide hydrochloride and 1.5 g. of sodium acetate are dissolved in 10 c.c. of water in a test tube. The mixture is

vigorously shaken and the test tube is placed in a boiling water bath for half to one hour. The cooled solution is filtered, the residue washed with water and recrystallised from water or aqueous alcohol.

(b) *For water insoluble compounds.* 1 c.c. of the aldehyde or ketone is dissolved in 10 c.c. of alcohol and water added until a faint turbidity appears, which is removed by the addition of a few drops of alcohol. Then 1 g. of semicarbazide hydrochloride and 1.5 g. of sodium acetate are added. Procedure (a) is then followed.

#### 4. Oximes :

The oximes of lower aliphatic aldehyde and ketones are usually difficult to isolate and purify owing to their low melting points. But the derivatives of higher molecular weight are well-defined crystalline compounds with sharp melting point.

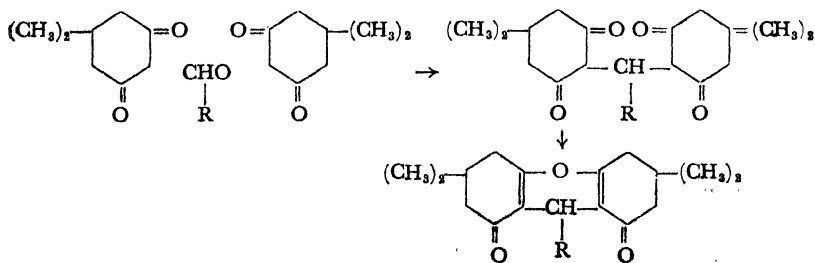
0.2 g. of the aldehyde or ketone is added to 3 c.c. of water containing 0.5 g. of hydroxylamine hydrochloride. A slight excess of sodium bicarbonate solution (5 to 6 c.c., 10%) is then added. If the carbonyl compound is insoluble in water just sufficient alcohol is added to give a clear solution. The mixture is heated on a water bath for 10 minutes and then cooled in ice. Precipitation of the derivative may be induced by scratching or adding a few drops of water. The solid is filtered, washed with cold water and recrystallised from water or aqueous alcohol.

#### 5. Oxidation products

Aromatic aldehydes are very readily oxidised to the corresponding acids by alkaline permanganate. The general procedure is precisely the same as that outlined for the oxidation of side chains of aromatic hydrocarbons. (p. 52).

#### 6. Dimedone derivatives

5 : 5-dimethyl cyclohexa- 1 : 3-dione (also known as dimedone, methone etc.) forms characteristic condensation products with aqueous alcoholic or acetic acid solution of aldehydes. Ketones do not react.



In glacial acetic acid, a further molecule of water is removed with formation of a xanthene derivative.

The aldehyde, if water soluble, is added to an aqueous solution of dimedone (0.2%) and the mixture is allowed to stand during several days or heated under reflux for one hour and then allowed to stand overnight at room temperature. If the aldehyde is not water soluble an alcoholic solution is added to an aqueous solution of dimedone, just sufficient alcohol added to give a clear solution, refluxed for one hour and left overnight at room temperature, the solid which separates is filtered and purified by recrystallisation from methyl or ethyl alcohol.

**Paraldehyde**, b.p. 124°.

Sharp odour ; does not usually show the properties of aldehydes.

**Formaldehyde** : Use dilute formalin for reaction.

*Semicarbazone* ; 169° ; *2 : 4-Dinitrophenyl hydrazone* 167°.  
Methone derivative ; 191°.

**Acetaldehyde**.

Prepare an aqueous solution of aldehyde (p. 61), from which one of the derivatives mentioned under acetaldehyde is obtained. Methone derivative : 140° ; *Semicarbazone* 152°.

**Salicylaldehyde**, b.p. 196°.

Colourless oil, faint phenolic odour ; gives intense violet colour with ferric chloride ; gives an insoluble bisulphite compound.

(1) *Salicylic acid*. Oxidation by alkaline permanganate (m.p. 158°).

(2) *Phenylhydrazone*, (m.p. 142°).

(3) *2 : 4-Dinitro-phenylhydrazone*, (m.p. 248°).

**Cinnamic aldehyde**, b.p. 220°d.

Odour of cinnamon ; with acid  $\text{KMnO}_4$  a smell of benzaldehyde is perceived.

(1) *Benzoic acid*. Oxidation with alkaline permanganate.

(2) *Phenylhydrazone*, (m.p. 168°).

(3) *Semicarbazone*, (m.p. 215°).

**Piperonal**, m.p. 37°.

Fragrant odour of heliotrope.

(1) *Oxime*, (m.p. 110°). Preparation : *vide* general methods.

(2) *6-Nitropiperonal*.

1 g. of finely powdered piperonal is added to 10 c.c. of  $\text{HNO}_3$  (sp. gr. 1.4) at  $0^\circ$  with shaking until completely dissolved. The mixture is poured into ice-water after half an hour. The precipitate is collected, washed and shaken with a strong solution of sodium bisulphite and filtered. On adding caustic soda to the filtrate, the 6-nitropiperonal separates out (yield, 0.7 g.). It is crystallised from alcohol; stout yellow needles, (m.p.  $98^\circ$ ). The portion insoluble in bisulphite crystallises from alcohol in long yellow needles, (m.p.  $145^\circ$ ).

**Methylethylketone**, b.p.  $80^\circ$ .

Mixes with water easily; does not give a bisulphite compound.

(1) 2 : 4-*Dinitrophenylhydrazone*, (m.p.  $115^\circ$ ).

(2) *Semicarbazone*, (m.p.  $135^\circ$ ).

**Benzophenone**, m.p.  $48^\circ$

(1) *Oxime*, (m.p.  $141^\circ$ ).

(2) *Semicarbazone*, (m.p.  $164^\circ$ ).

(3) 2 : 4-*Dinitrophenylhydrazone*, (m.p.  $229^\circ$ ).

**Cyclohexanone**, b.p.  $155^\circ$ .

Peppermint odour.

(1) *Oxidation to adipic acid*. Oxidise 1 c.c. as usual with 30 c.c. of sodium dichromate mixture (see appendix) and boil under reflux for 5 minutes. Cool, filter, wash the solid acid free of chromic salts. Crystallise from very little water. Determine its m.p. ( $150^\circ$ ).

(2) *Semicarbazone*, (m.p.  $166^\circ$ ).

### Phenols

The commoner derivatives for phenols are:—

1. Phenoxy-acetic acids;
2. Acetyl or benzoyl derivatives;
3. Nitration or bromination products; and
4. Picrates.

**Preparation of phenoxy-acetic acids.** These, in many cases, are solid crystalline substances with definite melting points, and serve as useful derivatives both in the case of the simpler phenols and their substitution products.

The method of preparation is fully described under Reactions, (p. 67). A list of the common phenoxy-acetic acids with their melting points is given in the Appendix.



**Acetyl derivatives.** The acetyl derivatives of common phenols are liquids or low melting solids which are not easy to crystallise. These are suitable only in a limited number of cases. In the case of the lower phenols, it is best to prepare the benzoyl, and in the case of the higher phenols, the acetyl derivatives.

*Preparation.* (a) To 1 g. of the phenol contained in a test-tube (6" × 1") fitted with an air condenser are added 2 to 3 g. of acetic anhydride and 1 g. of freshly fused sodium acetate or 5 drops of concentrated sulphuric acid to hasten the reaction, and the mixture kept gently boiling for 15 minutes. The liquid is cooled and poured into cold water (20 c.c.) to decompose the excess of acetic anhydride and the acetate which separates is re-crystallised.

(b) Dissolve the compound to be acetylated in an aqueous solution of slightly more than the required amount of sodium or potassium hydroxide, add crushed ice and then pour in an equivalent amount of acetic anhydride. After shaking for some time the acetylated product separates in a practically pure condition, after the addition of a mineral acid if the solution is alkaline.

**Benzoyl derivatives.** *Schotten-Baumann method.* 1 g. of the phenol is dissolved in 5 c.c. of acetone and the benzoylation proceeded with. (p. 66).

**p-Toluenesulphonates.** 1 c.c. of the phenol or 1 g. if solid, and 2 g. of p-toluenesulphonic chloride are dissolved in 5 c.c. of acetone by warming in a flask. The mixture is cooled and 30 c.c. of sodium hydroxide (2N) are added, the flask is corked and the contents shaken vigorously for 10 minutes. The solid is filtered, washed with water and the excess of the acid chloride decomposed by boiling with 30 c.c. of sodium hydroxide for 10 minutes. An equal volume of water is added, the flask is cooled, and the contents shaken till the derivative solidifies. It is recrystallised from alcohol or petroleum-ether (care).

**Bromination.** The majority of phenols are readily brominated on treatment with saturated bromine water, with the immediate precipitation of the insoluble polybromo-derivatives. These are best crystallised from alcohol.

**Nitration.** Phenols are more readily nitrated than the hydrocarbons, but the procedure for nitration is similar.

**Preparation of polynitro-derivatives.** 0.5 g. of the phenol is dissolved in 1-2 c.c. of cold concentrated sulphuric acid and the solution poured slowly into 6 c.c. of the nitration mixture, containing equal volumes of concentrated nitric and sulphuric acids. Whether cooling or heating is necessary, depends on the nature of the phenol. Where there is a tendency for the reaction to become violent and form tarry matter, cooling in ice is essential; otherwise warming on a water-bath for a few minutes will be helpful in completing the reaction. The mixture is poured after cooling into ice-water and the nitro-derivative crystallised from dilute alcohol with the addition of a few drops of concentrated hydrochloric acid.

**Picrates.** The picrates of phenols are prepared by methods quite similar to those adopted for the preparation of picrates of cyclic hydrocarbons. Only a few phenols give picrates. The preparation of picrates should be attempted only when other derivatives are difficult to obtain. The picrates prepared are recrystallised from the same solvent which has been used in their preparation. (For the melting points of picrates, see Appendix.)

**m-Cresol**, b.p. 203°.

(1) 2 : 4 : 6-*Trinitro-m-cresol*, (m.p. 106°).

4 to 5 drops of the cresol dissolved in 2 c.c. of concentrated sulphuric acid is poured with stirring into a mixture of 3 c.c. of concentrated nitric acid and 3 c.c. of concentrated sulphuric acid contained in a boiling tube and heated for ten minutes on a boiling water-bath. The contents are cooled and poured into ice-water and the precipitate crystallised from water to which a few drops of concentrated hydrochloric acid have been added.

(2) *m-Hydroxy-benzoic acid* by oxidation with alkaline permanganate, (m.p. 200°).

(3) *m-Cresoxy acetic acid*, (m.p. 103°).

**o-Cresol**, m.p. 35° ; b.p. 190°.

1% aqueous solution gives a violet colour with neutral ferric chloride.

(1) *Salicylic acid*, by oxidation with permanganate, (m.p. 158°).

(2) *Picrate*, (m.p. 88°). Orange-yellow needles of the picrate are obtained by the usual method.

(3) *Dibromo-derivative* (m.p. 56°).

Prepared by treating with saturated bromine water and recrystallising from alcohol.

(4) *o-Cresoxy acetic acid*, m.p. p. 151-152.

**p-Cresol**, m.p. 35° ; b.p. 201°.

Blue colour with ferric chloride.

(1) *Benzoate*, (m.p. 71°). Schotten-Baumann method.

(2) *Tetrabromo-derivative*, (m.p. 108°).

(3) *p-Cresoxy acetic acid*, (m.p. 135-136°).

**Thymol**, m.p. 49°.

Insoluble in water. Phthalic anhydride fusion gives a blue colour.

*Trinitro-thymol* (m.p. 109°). Preparation like the trinitro-m-cresol.

## Carbohydrates

### Sugars

The only convenient derivatives to prepare in the case of sugars are (1) osazones and (2) acetyl derivatives. The melting points of the osazones of the commoner sugars centre round 200°, so that the mere determination of a melting point is of little value in distinguishing the osazones from each other. They may be distinguished, however, by examining the crystalline forms under the microscope. The simple hydrazones are almost always soluble in water.

### Osazones

- 0.2 g. of the sugar, 0.4 g. of phenylhydrazine hydrochloride,  
 ○ 0.6 g. of sodium acetate crystals and 4 c.c. of distilled water are mixed in a test-tube and heated on a boiling water-bath for a period of from 1 minute to 1 hour. The osazones of maltose and lactose do not crystallise from hot solutions while the others separate out. The solution should always be cooled for some time, before arriving at a definite conclusion. When the sample of sugar is pure, the following intervals of time (in minutes) are observed as measured from the moment the tube is immersed in the boiling water to the appearance of the osazone: mannose 0.5-1; fructose, 1-2; glucose, 4-5, xylose, 6-8; arabinose 9-10; galactose, 14-16; and lactose and maltose, on boiling.

**Acetyl derivatives**

0.5 g. of the sugar is heated with 8-9 c.c. of acetic anhydride and 1 g. of freshly fused sodium acetate for about half an hour using an air condenser. The product is kept in contact with water (25 c.c.) for some time to decompose the excess of anhydride and the solid recrystallised from plenty of boiling water or dilute alcohol.

**Mucic acid**

Galactose and lactose yield the insoluble mucic acid on oxidation with nitric acid.

1 g. of the sugar is treated with 10 c.c. of nitric acid (1.15 sp. gr., *i.e.*, 25%) in a porcelain basin and evaporated on a water-bath to a syrupy consistency. This is rubbed with 10 c.c. water and the precipitated mucic acid is purified by dissolving in dilute sodium hydroxide (2N) and reprecipitating with dilute hydrochloric acid. The potassium salt is prepared as described under preparations and observed under the microscope.

A determination of the specific rotation of the sugar is also useful for purposes of confirmation.

**d-Glucose** (Dextrose), m.p.  $146^{\circ}$ , if anhydrous,  $[\alpha]_D$  in water,  $+109^{\circ}$  immediately after solution, falling to a constant value of  $+52.8^{\circ}$  after about 4 hours.

(1) *Osazone* (m.p.  $205^{\circ}$ ).

(2) *Penta-acetate* (m.p.  $111^{\circ}$ ). Preparation, *vide* reactions, (p. 86.)

**Fructose** (Laevulose), m.p.  $95-105^{\circ}$ ; rarely met with except as a syrup.  $[\alpha]_D$  in water,  $-106^{\circ}$  immediately after solution, falling to  $-95^{\circ}$  after half an hour.

*Glucosazone* (m.p.  $205^{\circ}$ ). (The crystals appear more quickly than with glucose.)

**Lactose**  $C_{12}H_{22}O_{11} + H_2O$ , m.p.  $203^{\circ}$  d.  $[\alpha]_D$  in water  $+87^{\circ}$  falling to  $52.5^{\circ}$  after 24 hours.

(1) *Lactosazone*, not precipitated in hot solution. (m.p.  $200^{\circ}$  d.)

(2) *Mucic acid*, (m.p.  $213^{\circ}$ ).

(3) *Octa-acetate*, (m.p.  $95-100^{\circ}$ ).

**Canesugar**, m.p.  $160^{\circ}$ .  $[\alpha]_D +66.5^{\circ}$  (Sucrose).

(1) *Octa-acetate*, (m.p.  $67^{\circ}$ ).

(2) *Glucosazone* after inversion, (m.p.  $205^{\circ}$ ).

### Carboxylic acids

These are often met with either as free acids or as the hydrolytic products of esters, amides, nitriles or anilides. They should be isolated in the pure state and the identity confirmed by the preparation of suitable derivatives such as—

- (1) Amides, imides (dibasic acids), anilides or toluidides.
- (2) Esters
- (3) S-Benzylthiuronium derivatives
- (4) Benziminazoles
- (5) Hydrocarbons or substituted hydrocarbons by decarboxylation.
- (6) Miscellaneous derivatives such as the nitro derivatives of aromatic acids.

#### 1. (a) Amides

Acids of low molecular weight, *e.g.*, acetic, propionic, butyric, isobutyric, etc., form highly soluble amides which are not therefore suitable derivatives to prepare. The amide of an aromatic acid may be prepared whenever possible as follows :—

0.5 g. of the solid acid is mixed in a dry tube with twice the amount of phosphorus pentachloride with a glass rod. The mixture is gently warmed for a minute, when it usually melts and gives off hydrogen chloride and when the reaction is complete, the tube is cooled and 3 c.c. of ice-water carefully added. In the case of aromatic acids, the acid chloride is not decomposed and may be isolated as an oil or as a solid. This is then treated with strong ammonia or preferably ground with solid ammonium carbonate when a vigorous reaction takes place and crystals of the amide separate out. It is recrystallised from water or dilute alcohol.

(b) **Anilides or Toluidides.** When the acid is free, the anilide or toluidide is prepared by gently heating to boiling, a mixture of the acid with slightly more than the equivalent quantity of the amine under reflux from 15 minutes to half an hour (see reactions for acids). On washing with dilute acid and boiling afterwards with dilute alcohol, the anilide or toluidide crystallises out.

When the acid is present as the sodium salt (resulting, say, from the saponification of an ester) the p-toluidide which is preferable to the anilide, is prepared as described under reactions for esters (p. 82).

The following procedure is also sometimes useful for preparing anilides or toluidides :—

0.5 g. of the acid (liquid or solid) is dissolved in 5 c.c. of light petroleum, 1 c.c. of thionyl chloride added and the solution boiled under reflux for about 15 minutes so as to convert the acid into the acid chloride. After cooling, an ethereal solution of the base is added little by little, and the dense precipitates of the hydrochloride and sulphite of the base are filtered and washed with hot light petroleum. Evaporation of the filtrate furnishes crystals of the pure anilide or toluidide.

## 2. Esters

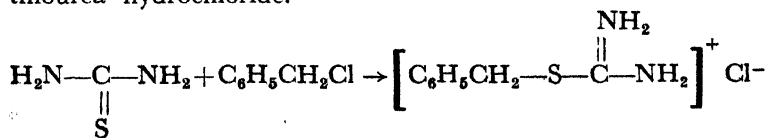
The methyl esters of some acids are solids and may be prepared as suitable derivatives either (a) by refluxing for 15-30 minutes 0.5 g. of the acid, 3 c.c. of methyl alcohol and 0.5 c.c. of concentrated sulphuric acid in a test-tube and pouring the reaction mixture after cooling into water, or (b) by converting the acid into the chloride by  $\text{PCl}_5$  and warming the acid chloride with methyl alcohol (*vide* p. 156).

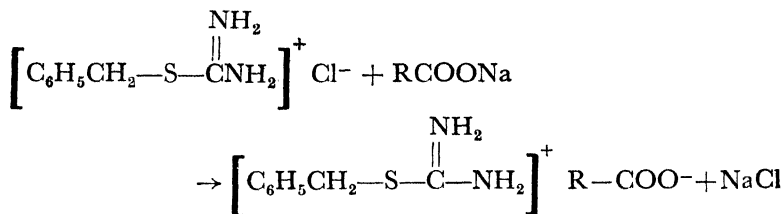
An excellent method of characterising acids is by preparation of p-bromophenacyl esters. This method is particularly advantageous because it does not require an anhydrous sample of the acid.

*Phenacyl ester.* 1 g. of the acid is added to 5 c.c. of water in a small flask and neutralised carefully with 10% sodium hydroxide solution. A few drops (or crystals) of the acid are then added till the solution is just acid to litmus. 10 c.c. of alcohol and 1 g. of p-bromophenacyl bromide are added; the mixture is then heated under reflux for one hour if the acid is monobasic, two hours if dibasic and three hours if tribasic. A few more c.c. of alcohol are added if a solid separates during refluxing. The solution is allowed to cool and the precipitated ester is purified by recrystallisation from alcohol.

## 3. S-Benzylthiuronium derivatives

The reaction between benzyl chloride and thiourea gives a compound known as S-benzylthiuronium chloride, or S-benzyl isothiurea hydrochloride.





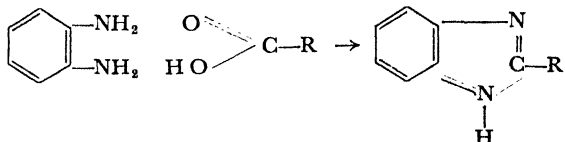
On mixing a solution of the alkali salt of a carboxylic acid with this reagent, the S-Benzylthiuronium derivative of the acid is formed rapidly. Crystallisation is effected from anhydrous solvents, (alcohols, dioxane) to prevent hydrolysis.

A solution of the acid (1 g.) in 10 c.c. water is carefully neutralised with aqueous sodium hydroxide using phenolphthalein as indicator, one or two drops of N—HCl are added, and then treated with a solution of S-Benzylthiuronium chloride (2 g.) in 10 c.c. of water. The mixture is placed in ice until the precipitation of the derivative is complete. It is then filtered and purified by crystallisation.

#### 4. Benziminazoles

When o-phenylene diamine is heated with fatty acids benziminazoles are formed. These are suitable for the characterisation of aliphatic monobasic acids.

1 g. of the acid and 1 g. of o-phenylenediamine are heated together under reflux for half an hour. The mixture is dissolved in hot alcohol and the unchanged acid neutralised (phenolphthalein) with potassium hydroxide solution. The 2-alkyl benziminazoles are obtained by cooling; if no solid derivative separates, the isolation is effected by ether extraction.



#### 5. Hydrocarbons

The soda-lime distillation is carried out as described under preliminary reactions and the resulting hydrocarbon in the case of carboxylic acids or phenol in the case of phenolic acids is identified by preparing derivatives under each group.

## 6. Miscellaneous derivatives

Nitration is carried out either by fuming nitric acid or by dilute nitric acid, depending on the individual acids ; concentrated sulphuric acid is not often used along with nitric acid.

Unsaturated acids in some cases give by bromine addition, dibromo compounds. No general procedure is possible. Specific instructions where such preparations are practicable, are given in their proper places.

**Propionic**, b.p.  $140^{\circ}$

(a) *Anilide*, (m.p.  $103^{\circ}$ ).

(b) *p-Toluidide*, (m.p.  $124^{\circ}$ ).

**Benzoic**, m.p.  $121^{\circ}$

(a) *m-Nitrobenzoic acid*. 0.1 g. of acid is nitrated with a mixture of 3 c.c. of fuming nitric and 2 c.c. of concentrated sulphuric acid at room temperature. The acid is recrystallised from dilute alcohol, (m.p.  $140^{\circ}$ ).

(b) *Benzamide*, (m.p.  $128^{\circ}$ ) (*vide* general methods of preparing derivatives for acids).

(c) *Benzanilide* (m.p.  $160^{\circ}$ ). (p. 83).

(d) *Benzo-p-toluidide*, (m.p.  $156^{\circ}$ ). (*vide* reactions).

**Salicylic**, m.p.  $158^{\circ}$

(1) *5-Nitro-salicylic acid* (m.p.  $226^{\circ}$ ). Nitration is carried out with dilute nitric acid (*vide* reactions).

(2) *Phenyl benzoate* (m.p.  $68^{\circ}$ ). Heating with soda-lime to get the phenol and converting into its benzoyl derivative.

(3) *Aspirin* (m.p.  $135^{\circ}$ ). By acetylating with acetyl chloride, in benzene solution. It is recrystallised from boiling water.

**Phthalic**, m.p.  $195^{\circ}$  d.

(1) *Anil*, (m.p.  $205^{\circ}$ ). (*vide* reactions).

(2) *Phthalimide*. 0.3 g. of the acid is heated strongly in a test-tube, the sublimate is scraped into another test-tube and heated with 1 g. of urea in a sulphuric acid bath. When the reaction is over, the product is washed with water and recrystallised from ether (m.p.  $233^{\circ}$ ).

**Succinic**, m.p.  $185^{\circ}$

(1) *Anilide*, (m.p.  $226^{\circ}$ ).

(2) *p-Toluidide*, (m.p.  $255^{\circ}$ ). (*vide* reactions).



**Isophthalic**, m.p. above  $300^{\circ}$ .

Slightly soluble in water ; gives benzene on heating with sodalime.

(1) *Dimethyl isophthalate*, (m.p.  $64^{\circ}$ ). 0.2 g. of acid and 0.6 g. of phosphorus pentachloride are heated carefully over a tiny flame till the mixture becomes a liquid. It is then cooled and warmed with 2 c.c. of methyl alcohol. On dilution with water the ester is precipitated and purified by recrystallisation from dilute methyl alcohol.

**Terephthalic**, sublimes ; insoluble in water.

(1) *Amide*, (m.p.  $265^{\circ}$ ). (*vide* general methods).

(2) *Dimethyl ester*, (m.p.  $140^{\circ}$ ). Preparation like the corresponding derivative for isophthalic acid.

### Esters

Esters are identified by hydrolysis either by alkalies or acids as described under reactions. For examination of the alcohol, alkaline hydrolysis is preferable. In the latter case, the acid is present as its alkali salt, which may some-times be precipitated. In acid hydrolysis, the acid, if insoluble, is precipitated on cooling. The solution after alkaline hydrolysis is carefully neutralised with acid (using an indicator). The solubility or insolubility of the acid is made evident during neutralisation. If the acid is insoluble and is precipitated, it is filtered and identified as described (p. 152). If the acid is soluble, the solid alkali salt is obtained by evaporation of the neutral liquid and converted into the anilide or toluidide (p. 152).

Very high boiling esters (above  $200^{\circ}$ ) which are insoluble in water hydrolyse slowly and prolonged refluxing may result in loss of a volatile alcohol. Such esters are best hydrolysed by a solution of potassium hydroxide in diethylene glycol. All but high boiling alcohols can be distilled from the reaction mixture in a pure state.

**Procedure for Hydrolysis.** (a) The ester (5 c.c.) is added to 40 c.c. of a 25% sodium hydroxide solution and refluxed. Simple esters boiling below  $110^{\circ}$  require about 30 minutes. Esters boiling between  $110^{\circ}$  and  $200^{\circ}$  require about two hours for complete saponification. The condenser is then set for distillation and the flask heated. About 10 c.c. of the distillate is collected and examined for the alcohol. The residual solution in the flask is acidified and the acid isolated suitably.

(b) (for high boiling esters). In a 25 c.c. distilling flask, 3 c.c. of diethylene glycol 0.5 g. of potassium hydroxide and 0.5 c.c. of water are placed. The mixture is heated gently until the alkali is dissolved, cooled and 1-2 g. of the ester is then added. The flask is heated gently and when only one liquid or one liquid and one solid phase are present, the mixture is heated more strongly and the distillate is collected in a cooled receiver. The alcohol is characterised suitably. The residue in the flask is diluted with water and worked up for the acid.

**Amide formation.** 0.5 c.c. of ester is treated with 5-10 c.c. of strong ammonia in a corked test-tube and vigorously shaken. The formation of amide depends upon the nature of the ester. If there is no immediate precipitation, the mixture is set aside for an hour. If the ester is insoluble in water, it may be just dissolved in the required amount of alcohol and saturated with ammonia gas. The solid amide is filtered off and crystallised from water or alcohol. Soluble amides may be recovered by extraction with chloroform.

**Ethyl oxalate**, b.p. 186°

- (1) *Oxamide* (*vide* reactions) sublimes without melting.
- (2) *Oxanilide* (m.p. 247°). By warming a few drops of the ester with an equal amount of aniline.

**Methyl salicylate**, b.p. 224°.

Violet colour with  $\text{FeCl}_3$ .

- (1) *Salicylic acid*, (m.p. 158°). By hydrolysis.
- (2) *Benzoyl derivatives*, (m. p. 82°). Schotten-Baumann method.

### Amines

Amines are highly reactive and therefore capable of giving a large variety of derivatives. The commoner derivatives prepared in the case of primary and secondary amines are :

- (1) Acetyl or benzoyl derivatives
- (2) Sulphonamides
- (3) Substituted ureas and thioureas
- (4) Schiff's bases
- (5) Picrates

In the case of tertiary amines the only possible derivatives are

- (6) Nitroso compounds (in the case of aromatic amines having the para position free)
- (7) Picrates
- (8) Quaternary ammonium salts.

### 1. (a) **Acetylation**

Acetylation may be done using either acetyl chloride or acetic anhydride. When acetyl chloride is used, generally in the case of feeble bases, it is best to have an indifferent solvent like ether or benzene. There is an immediate precipitation of the base hydrochloride, while the acetyl derivative remains in solution and is recovered by evaporation of the solvent. In acetylating with acetic anhydride which is most commonly used, the base is suspended in cold water and shaken with nearly twice the amount of acetic anhydride. The acetyl compound separates soon in a very pure crystalline condition. If this method does not succeed, the amine (1 g.) and acetic anhydride (2 c.c.) are boiled for 5 minutes with the addition of a dehydrating agent like fused sodium acetate or zinc chloride (0.5 g.) or a few drops of pyridine. The solution is poured into water (10 c.c.) and the acetyl derivative which separates out on standing is crystallised from dilute alcohol.

(b) **Benzoylation.** Benzoylation is carried out by the Schotten-Baumann method.

Sometimes it is easier to carry out the benzoylation of an amine by heating it with benzoyl chloride in benzene or pyridine or in a high boiling indifferent solvent like nitrobenzene, the latter being removed by steam distillation.

(c) **Hydrochlorides :** In the case of the simpler aromatic amines, the amine hydrochlorides themselves serve as useful derivatives possessing definite melting points and volatilising without much decomposition. They may be prepared by simply rubbing together a few drops each, of concentrated hydrochloric acid and the amine or by passing dry hydrogen chloride into a solution of the amine in dry ether or benzene. The precipitated hydrochloride is filtered, washed with a little dry ether or benzene and quickly dried. It can be purified by crystallisation.

### 2. **Sulphonamides**

Benzene sulphonyl chloride and p-toluene sulphonyl chloride have been widely used. A typical procedure is as follows : A solu-

tion of the sulphonyl chloride (1 g.) in acetone (5 c.c.) is added to a solution of the amine (1 g.) in 1 c.c. pyridine. If no reaction appears to take place on shaking, the mixture is heated on a water-bath during twenty minutes, cooled and poured into dilute hydrochloric acid (25 c.c. 5%). The precipitate is filtered off, washed with cold water and recrystallised from aqueous alcohol.

### 3. Substituted ureas and thioureas

Primary and secondary amines react smoothly with aryl isocyanates at room temperature or more rapidly by heating equimolecular proportions in a non-hydroxylic solvent. The reaction should be carried out under anhydrous conditions.

A solution of 1 g. of the amine in 10 c.c. dry petroleum ether (b.p. 80-120) is added to the aryl isocyanate 1 g. in the same solvent (15 c.c.) and the mixture is heated under reflux for thirty minutes. The solution is filtered off. The solid which separates on cooling is filtered, washed with petroleum ether and recrystallised from the same solvent.

Isothiocyanates react with primary and secondary amines to give thioureas. Isothiocyanates do not react with water or alcohols and are therefore superior agents for characterisation of amines.

A solution of 0.2 g. of the amine in 5 c.c. of alcohol is added to 0.2 g. phenyl isothiocyanate in 5 c.c. alcohol. If no reaction takes place at room temperature the mixture is warmed for fifteen minutes on a water-bath and cooled. The precipitated thiourea is filtered, washed with ice-cold alcohol and crystallised from the same solvent.

### 4. Schiff's bases

The condensation of an aldehyde and a primary amine takes place readily yielding a weakly basic compound known as a Schiff's base. 2:4-Dinitrobenzaldehyde is the most suitable reagent for this purpose.

Hot alcoholic solutions of the amine (1 mol.) and 2:4-dinitrobenzaldehyde (1.1 mol. for each amino group) are mixed and a few drops of glacial acetic acid added. The solid which separates on cooling is filtered off, washed with alcohol and recrystallised from alcohol or benzene.

### 5. Picrates

The picrates are the most convenient derivatives to prepare for the tertiary amines. They are as a rule insoluble in water

and sparingly so in alcohol. They are prepared by the general method.

### **p-Nitroso compounds**

These are possible only in the case of tertiary amines of the aromatic series with a free para position and are therefore only of limited applicability.

#### **p-Toluidine**, m.p. 43°.

Characteristic peculiar odour.

(1) *Acetyl p.-toluidide*, (m.p. 146°)

(2) *Benzo-p-toluidide*, (m.p. 155°)

#### **α-Naphthylamine**, m.p. 49°.

Unpleasant smell ; solution in hydrochloric acid gives a blue precipitate with ferric chloride.

(1) *Acetyl derivative*, (m.p. 159°)

(2) *Benzoyl derivative*, (m.p. 160°).

(3) *Picrate*, (m.p. 161°).

#### **β-Naphthylamine**, m.p. 110°.

White scales, odourless, sparingly soluble in hot water, soluble in alcohol, does not give any colour with ferric chloride.

(1) *Acetyl derivative*, (m.p. 132°)

(2) *Benzoyl derivative* (m.p. 162°)

(3) *Hydrochloride*, (m.p. 260°).

Prepared by the general method (p. 158) using 0.3 g. in 4 c.c. benzene.

#### **Ethyl aniline**, b.p. 205°.

(1) *Hydrochloride*, (m.p. 176°).

(2) *Tetranitro-derivative*, (m.p. 95-96°).

#### **Diphenylamine**, m.p. 54°.

Lustrous plates. Insoluble in dilute acids. Solution in concentrated  $\text{H}_2\text{SO}_4$  gives intense blue colour with a trace of nitric acid or nitrates.

(1) *Nitrosamine*. 0.2 g. of the amine is dissolved in 5 c.c. of alcohol and 2 c.c. of concentrated hydrochloric acid are added. The mixture is cooled in ice and a slight excess of a saturated solution of sodium nitrite is added. The solution becomes green and a yellow precipitate gradually separates. The mixture is diluted with water and the precipitate filtered, dried and recrystallised from light petroleum, (m.p. 60°).

(2) *Acetyl derivative*, (m.p. 106°).

(3) *Diphenylamine tetrabromide* (m.p. 183°). To an alcoholic solution of 0.1 g. of the amine a slight excess of bromine is added and the precipitate recrystallised from benzene.

**Dimethylaniline**, b.p. 193°C

- (1) *p*-nitroso-derivative, (m.p. 85°), *vide* reactions.
- (2) *Methiodide*, (m.p. 220° d.).
- (3) *Picrate*, (m.p. 162°).

**Diethylaniline**, b.p. 216°

- (1) *Picrate*, (m.p. 142°).
- (2) *p*-Nitrodiethylaniline, (m.p. 78°)

4-5 drops of the base are dissolved in 4 c.c. of glacial acetic acid, concentrated nitric acid (6 drops) added drop by drop and the mixture warmed on a tiny flame until it shows signs of darkening, when it is cooled and poured into ice-water. The precipitate is filtered and recrystallised from alcohol. To hasten crystallisation the test-tube should be shaken vigorously.

**Nitrogen compounds other than Amines**

These are usually of two types : (a) those containing the nitro group which are easily reduced to the amines by suitable reducing agents and (b) those which are easily hydrolysed such as the nitriles, the acid amides or imides.

**Nitro compounds.** The mono-nitro compounds are best identified by reducing the nitro group in acid solution to the primary amines. The latter can be isolated and characterised by preparing the acetyl or benzoyl derivatives or (if aromatic) by diazotising and coupling with  $\beta$ -naphthol in alkaline solution.

The reducing agents that are very effective are :—

- (1) sodium hyposulphite in weak alkaline solution.
- (2) tin powder or foil with (1 : 1) hydrochloric acid.
- (3) zinc dust and dilute hydrochloric acid or acetic acid.

**Procedure.** 0.2 g. of the substance dissolved in water, or if insoluble, in dilute alcohol, is heated under reflux with 1 g. of any of the above reducing agents over a small flame or on a boiling water-bath. Sodium hyposulphite is preferable in many cases as it leaves behind only sodium chloride and a little free sulphur on acidifying. The amine is liberated by adding alkali and extracted twice with ether. The ether extract is shaken with dilute hydrochloric

acid; The amine is liberated from the acid solution as before. The amine is then acetylated or benzoylated in aqueous solution.

The aromatic mono-nitro compounds may further be identified by preparing solid poly-nitro compounds by the usual methods of nitration outlined under hydrocarbons.

The nitrogroups in poly-nitro compounds may be reduced in stages by the use of aqueous or alcoholic sodium sulphide or alcoholic ammonium sulphide. The reduction may also be effected by suspending the nitrocompound in a large amount of water and adding a solution of sodium sulphide, while the liquid is kept gently boiling. The precipitated sulphur is filtered off and the nitranilines purified by solution in dilute hydrochloric acid, filtering the solution and reprecipitating by the addition of ammonia (See preparation of m-nitraniline).

### Nitriles and Amides

The derivatives that are easiest to prepare are :—

(1) *the corresponding acids obtained by hydrolysis.* The amides and nitriles of fatty acids are easily hydrolysed by 15% aqueous sodium hydroxide. Ammonia is evolved and the sodium salt of the acid is obtained. Further procedure to isolate the acid or prepare a derivative of the acid is the same as that outlined under esters.

In the case of aromatic compounds which are more difficult to hydrolyse, the following procedure is useful—

(a) *Hydrolysis with concentrated hydrochloric acid.* 1 g. of the substance is boiled in a small flask fitted with an air condenser, with 10-15 c.c. of concentrated hydrochloric acid for half an hour. On cooling, the acid, if insoluble, is obtained as a solid and is identified as usual. If no solid separates, the liquid is neutralised with sodium hydroxide and evaporated and from the solid sodium salt, the toluidide is prepared.

(b) *Hydrolysis with sulphuric acid.* A mixture of equal volumes of concentrated sulphuric acid and water is more effective in some cases. The procedure is the same as that described under (a). Trial experiments should be made in test-tubes before deciding on the most suitable concentration of acid.

(c) *Hydrolysis with alcoholic potash.* In obstinate cases, 0.5 g. of the amide is boiled under reflux with 10 c.c. of 15% alcoholic

potash for an hour. The alcohol is removed by evaporation and the potassium salt of the acid is treated exactly as described under esters.

(2) *Anilide*. Amides are readily converted into anilides by heating with aniline, ammonia being evolved.

(3) *Amides*. Nitriles are converted into amides by oxidation in alkaline solution with hydrogen peroxide, (cf. Benzonitrile).

### **Anilides**

(1) *Hydrolysis*. These are hydrolysed by any of the methods described above. Hydrolysis of anilides with caustic alkalies is usually very slow. Acid hydrolysis with 70% sulphuric acid should be carried out. A 70% sulphuric acid is prepared by adding 40 c.c. of concentrated sulphuric acid to 30 c.c. of water. Each gram of the anilide requires roughly 10 c.c. of the above acid and when the hydrolysis is carried out in acid solution, the base remains in solution while the acid is in the free state. If the acid is insoluble, it is precipitated. The acid is separated by filtration and purified by solution in sodium bicarbonate solution and reprecipitation. From the filtrate the free base is liberated by adding 5 to 10% sodium hydroxide and identified by the usual tests. If the acid is soluble, the liquid after hydrolysis is neutralised to recover the base and at the same time to convert the acid into its sodium salt. The base is removed by extraction with a solvent and the solution of the sodium salt of the acid is evaporated to dryness and treated as usual.

(2) *Bromoderivatives*. Some anilides are readily brominated in acetic acid solution (acetanilide) and the bromocompounds are useful for purposes of identification.

(3) *Nitration*. Nitrocompounds are obtained by nitrating in the cold with fuming nitric acid as described under derivatives for hydrocarbons.

### **Nitrocompounds**

**o-Nitrotoluene**, b.p. 220°.

Odour like that of nitrobenzene.

(1) 2:4-Dinitrotoluene, (m.p. 70°).

0.5 c.c. of the liquid is nitrated as usual with 4 c.c. of a mixture of fuming nitric acid and concentrated sulphuric acid (*vide* Toluene).

(2) o-Toluidine by reduction with tin and hydrochloric acid.



**p-Nitrotoluene**, m.p. 54°

(1) 2 : 4-*Dinitrotoluene*.

Using 0.1 g. of substance nitration is carried out as under o-nitrotoluene.

(2) p-Nitrobenzoic acid. Place 1 g. of the substance in a 100 c.c. round-bottomed flask, add 2-3 g. of finely powdered potassium permanganate, 40 c.c. water, five drops of sodium hydroxide (2N) and a few pieces of porous porcelain. Boil under reflux for about an hour or till the purple colour nearly disappears. Filter off the  $MnO_2$ , pass  $SO_2$ , or acidify the filtrate with conc. HCl. Filter off the solid and wash with cold water. Crystallise the solid from water or dilute alcohol. It may further be converted into the amide by the usual methods. Acid (m.p. 241°), amide (m.p. 201°).

*N.B.* (The chloro and bromo toluenes are oxidised to the corresponding acids in the same manner).

**m-Dinitrobenzene**, m.p. 90°.

(1) *m-Nitraniline*, (m.p. 114°).

(2) *m-Phenylenediamine* by reduction with tin and hydrochloric acid. (m.p. 63°).

**o-Nitrophenol**, m.p. 44°.

Yellow ; volatile in steam.

(1) *o-Aminophenol*. (m.p. 174°).

(2) *Picric acid*. Preparation by usual methods of nitration, (m.p. 122°).

(3) *Benzoate*, (m.p. 142°).

**p-Nitrophenol**, m.p. 114°.

(1) *p-Aminophenol*. (m.p. 184°).

(2) 2 : 4-*Dinitrophenol*, (m.p. 114°). Nitration with nitric acid, (2:1).

(3) *Picric acid*, (m.p. 122°).

### Nitriles

**Acetonitrile**, b.p. 81°.

Soluble in water.

(1) *Acetic acid* by hydrolysis and conversion into acetanilide or p-acettoluidide.

**Benzonitrile**, b.p. 190°.

Odour resembling nitrobenzene.

(1) *Benzoic acid*, (m.p. 121°), by hydrolysis with 50% sulphuric acid.

(2) *Benzamide*, (m.p. 128°).

**Anilides****Acetanilide**, m.p. 114°.

(1) *p*-*Bromoacetanilide*, (m.p. 167°), or *p*-bromoaniline, (m.p. 66°). (*vide* reactions).

(2) *p*-*Nitroacetanilide*, (m.p. 210°) by nitration with fuming nitric acid and sulphuric acid mixture in ice.

**Benzanilide**, m.p. 161°.

(1) *Benzanilide*. Hydrolyse 1 g. of anilide with 10 c.c. of 70% sulphuric acid. Some benzoic acid may crystallise in the condenser as it is volatile in steam.

(2) *p*-*Bromobenzanilide*, (m.p. 204°). Preparation (*vide p*-bromoacetanilide).

**Amides****Acetamide**, m.p. 82°.

Very hygroscopic, peculiar odour, soluble in water.

(1) *Acetanilide*. Heating with aniline (m.p. 114°).

**Benzamide**, m.p. 128°.

(1) *Benzoic acid*. Hydrolysis.

(2) *Benzanilide*. Heating with aniline (m.p. 160°).

**Urea**, m.p. 132°.

(1) *Oxalate*, (m.p. 171°).

(2) *Carbanilide*, (m.p. 238°).

**Salicylamide**, m.p. 138°.

Violet-red colour with ferric chloride.

(1) To 0.2 g. of the substance add 5 drops of concentrated sulphuric acid, and an equal volume of methyl alcohol. Warm and pour into dilute sodium carbonate. Odour of oil of wintergreen is perceived.

(2) Hydrolysis.

0.5 g. of substance is refluxed with 10 c.c. of water and 5 c.c. of concentrated sulphuric acid for half an hour. On cooling the acid is precipitated. It is recrystallised and its m.p. determined. The filtrate is tested for an ammonium salt as usual.

**Phthalimide**, m.p. 233°.

- (1) *Phthalic acid*, (m.p. 195°), hydrolysis.
- (2) *Phthalanil*, (m.p. 205°). Heat with aniline.

**Oxamide**, m.p. 418°.

- (1) *Oxanilide*, (m.p. 245°). Heat with aniline.

### Simple Halogen Compounds

**Aliphatic halogen compounds including aromatic compounds with halogen in the side-chains.**

(1) *Isolation of the corresponding alcohol and conversion into the 3 : 5-dinitrobenzoate, or p-nitrobenzoate.* 1 g. of the substance is boiled under reflux with 10-15% alkali and the alcohol separated by distillation as aqueous solution in the case of miscible alcohols. Immiscible alcohols like amyl and benzyl alcohols can be separated by suction pipettes. The alcohols are identified by conversion into the dinitrobenzoates, etc.

(2) *Pyridinium salts or quaternary compounds with aromatic tertiary amines like dimethylaniline.*

(3) *Phenolic ethers.* Solid derivatives are obtained with  $\beta$ -naphthol.  $\beta$ -Naphthol is dissolved in alcohol, and the required amount of alkali is then added. The substance is boiled under reflux with the above solution and after removal of the alcohol by evaporation, the ether is obtained and crystallised from very dilute alcohol.

Aromatic compounds containing halogen in the side-chain are easily oxidised to carboxylic acids by alkaline permanganate. The procedure is the same as that for hydrocarbons.

**Aromatic halogen hydrocarbons with halogen in the nucleus.** The halogen in these compounds is not very reactive. The only derivatives possible are the nitroderivatives or the sulphonamides. The methods of preparation are precisely the same as those outlined under hydrocarbons.

**Acid halides.** Amides, anilides or esters are the usual derivatives prepared.  $\beta$ -Naphthyl esters are mostly solids and hence they are preferred. For methods of preparation refer to reactions of halogen compounds.

**Benzyl chloride**, b.p. 179°. Sharp odour.

- (1) *Benzoic acid.* Oxidation by alkaline permanganate.

(2) *Nitroderivative* : To 1 c.c. of fuming nitric acid contained in a test-tube are added five drops of the liquid with cooling in ice-water during the addition. When the tube is removed from the bath, the mixture becomes warm. After an interval of 5 minutes the mixture is poured into ice-water and the solid filtered and crystallised from alcohol, the oily ortho-nitro compound remaining in solution, (m.p.  $71^{\circ}$ ).

(3)  *$\beta$ -Naphthyl methyl ether*, (m.p.  $99^{\circ}$ ). Preparation as per general instructions.

**Bromobenzene**, b.p.  $157^{\circ}$

(1) *p*-Nitrobromobenzene, (m.p.  $126^{\circ}$ ).

(2) 2:4-Dinitrobromobenzene (m.p.  $75^{\circ}$ ).

(3) *p*-Bromobenzenesulphonamide, (m.p.  $160^{\circ}$ ).

**Iodobenzene**, b.p.  $188^{\circ}$

*p*-Nitriodobenzene, (m.p.  $171^{\circ}$ ).

**Methyl iodide**, b.p.  $43^{\circ}$

(1)  *$\beta$ -Naphthyl methyl ether*, (m.p.  $70^{\circ}$ ).

(2) *Pyridine methiodide*, (m.p.  $117^{\circ}$ ). *vide* reactions of pyridine.

**Ethyl iodide**, b.p.  $72^{\circ}$

(1) *Dimethylethylphenylammonium iodide*, (m.p.  $136^{\circ}$ ). (See Dimethylaniline.

(2) *Pyridin ethiodide*, (m.p.  $90^{\circ}$ ).

**Acetyl chloride**, b.p.  $52^{\circ}$

Pungent odour fuming in air.

(1) *Anilide*, (m.p.  $114^{\circ}$ ).

(2) *p*-Toluidide, (m.p.  $153^{\circ}$ ).

**Benzoyl chloride**, b.p.  $197^{\circ}$

Sharp odour ; stable in the presence of water.

(1) *Benzoic acid*. Hydrolysis.

(2) *Anilide*, (m.p.  $160^{\circ}$ ).

(3) *p*-Toluidide, (m.p.  $158^{\circ}$ ).

**Sulphur compounds.** The most familiar sulphur compounds are the free acids or metallic salts of sulphonic acids, the sulphonyl chlorides and sulphonamides. The general properties have been indicated already and the possible derivatives are very limited.

In the case of sulphonic acids, the sulphonyl chlorides and sulphonamides, both of which have definite melting points, can be

prepared as described before. Sulphonic acids can be characterized by the preparation of the S-benzyl isothiuronium salts. In addition, the phenols may be obtained by alkali fusion and converted into benzoates (*vide* reactions). Sulphonyl chlorides are converted into sulphonamides, while sulphonamides can be identified only by their decomposition products.

**Benzenesulphonic acid**, m.p.  $65^{\circ}$

Very soluble in water ; solution strongly acidic.

(1) *Sulphonamide*, (m.p.  $153^{\circ}$ ). Preparation from the sodium salt, *vide* reactions.

(2) *Sulphonanilide*, (m.p.  $105^{\circ}$ ).

(3) *Phenol*. After fusion with potash, phenyl benzoate is prepared.

**p-Toluenesulphonic acid**, m.p.  $92^{\circ}$

(1) *Sulphonyl chloride*, (m.p.  $69^{\circ}$ ).

(2) *Amide*, (m.p.  $137^{\circ}$ ).

**Benzenesulphonyl chloride**, b.p.  $246^{\circ}$ .

Insoluble in water.

(1) *Amide*, (m.p.  $153^{\circ}$ ).

(2) *Anilide*, (m.p.  $105^{\circ}$ ).

**p-Toluenesulphonyl chloride**, m.p.  $69^{\circ}$

Fuming in air, decomposed only on boiling with water.

(1) *Amide*, (m.p.  $137^{\circ}$ ).

(2) *Anilide*, (m.p.  $103^{\circ}$ ).

**p-Toluenesulphonamide**, m.p.  $137^{\circ}$

Colourless plates ; boiled with alkali gives ammonia and the sulphonic acid.

(1) *Methylation* with dimethyl sulphate gives the dimethyl derivative, (m.p.  $79^{\circ}$ ).

(2) *Benzyl derivative*, (m.p.  $88^{\circ}$ ).

**Benzenesulphonamide**, m.p.  $153^{\circ}$ .

Colourless needles soluble in hot water.

(1) *Dimethyl derivative*, (m.p.  $88^{\circ}$ ).

(2) *Benzyl derivative*, (m.p.  $88^{\circ}$ ).

## CHAPTER VII

### MODEL ANALYSES OF SIMPLE ORGANIC SUBSTANCES

There is a common tendency among students when given a substance for analysis, to hazard a guess about its identity on the basis of a few tests hastily carried out, taken in conjunction with the melting or boiling point of the substance. It is needless to say that such an approach almost invariably leads to wrong conclusions. Preliminary reactions detailed in Chapter V must all be carried out without omission, followed by all the reactions for functional groups, the preparation of suitable derivatives being the last step. Consultation of books for identification purposes should be taken up only after the completion of all these stages. In the case of mixtures, the preliminary experiments yield information of value in devising a separation procedure. The entire analysis, including the preliminary tests should then be carried out with each of the pure components.

In the following pages, model analyses of some simple substances and of mixtures are recorded. Only the salient features about these substances are reported, because of limitations of space, but the student should write out a complete record, including all the tests carried out, whether the results are positive or negative.

#### Substance 1

A colourless liquid with an aromatic odour insoluble in water, b.p. 154-155°.

The substance burnt with a highly sooty flame and so was rich in carbon. May be aromatic in nature.

#### Detection of elements

Nitrogen, sulphur, halogens were absent.

#### Preliminary reactions

It had no action on moist litmus and was insoluble in cold sodium hydroxide or bicarbonate.

It dissolved easily in ice-cold concentrated sulphuric acid. After keeping for some time and then pouring into ice-water, the original liquid was liberated. Hence it might be an ether or a hydrocarbon which does not undergo sulphonation readily.

Tests for the reactive compounds of the class containing carbon, hydrogen and oxygen were not answered.

To a few drops of the liquid in a dry test-tube a clean bit of sodium was added, and gently warmed. A few bubbles were given off at first after which the sodium remained unattacked. When a few granules of phosphorus pentachloride were added no reaction took place. Hence, the presence of an ether or a hydrocarbon was confirmed.

To find out whether it was an aromatic ether, 0.5 c.c. of liquid was mixed with 5 c.c. of hydriodic acid (sp. gr. 1.8) in the small Zeisel apparatus and heated at  $130^{\circ}$  with a slow current of carbon dioxide passing through. The vapour was passed into a tube containing 1 c.c. of dimethylaniline. A crystalline solid was obtained. This was treated with ether, filtered and crystallised from a little methyl alcohol. It melted and decomposed at  $226^{\circ}$ . Trimethylphenylammonium iodide decomposes at  $228-229^{\circ}$ .

The residue in the tube was treated with sodium bisulphite till it became colourless ; a few c.c. of 2N sodium hydroxide were added to keep the liquid alkaline and then a few drops of benzoyl chloride. The test-tube was corked and shaken. The benzoyl derivative of the phenol separated as a solid. On recrystallisation from alcohol it melted at  $67^{\circ}$  (m.p. of phenyl benzoate  $68^{\circ}$ ).

Hence the given substance may be anisole.

### **Confirmatory test by preparing a derivative**

To 2 c.c. of concentrated sulphuric acid in a test-tube six drops of the ether were added and dissolved by gentle shaking. The test-tube was immersed in a beaker containing ice. Concentrated nitric acid, about 1 c.c. was added drop by drop with frequent shaking and cooling. The mixture was kept in ice for about five minutes. On adding cold water a yellow oily substance separated which, on adding some fragments of ice, slowly solidified to a crystalline mass. The substance crystallised from alcohol in fine needles and melted at  $85^{\circ}$ . The melting point of 2 : 4-dinitro-anisole is  $86^{\circ}$ .

Hence the original substance was ANISOLE.

### **Substance 2**

A colourless liquid with a faint spirituous odour. Most of the liquid distilled between  $82-83^{\circ}$ .

**Test for elements**

Nitrogen, sulphur, halogens absent.

**Preliminary reactions**

(1) The liquid dissolved in water easily and the solution was neutral to litmus.

(2) A drop of the liquid introduced at the tip of a glass rod into the flame burnt with a slightly luminous flame. Probably aliphatic in nature.

(3) Heated a few drops of the liquid with 1 c.c. of concentrated sulphuric acid. The solution became slightly brown and a little sulphur dioxide was given off.

(4) There was no reaction with sodium hydroxide or carbonate.

(5) (a) Added a few drops of the liquid to 1 c.c. of cold dilute 1% alkaline permanganate. Instantaneous oxidation took place with precipitation of manganese dioxide. This showed the presence of an easily oxidisable or unsaturated substance.

(b) Added a few drops of the liquid to a few drops of bromine in carbon tetrachloride. There was no action showing that the substance was not unsaturated.

**Classification reactions**

(6) The substance did not show the reactions of aldehydes, ketones or acids. The possibility of its being an ester was eliminated as it was easily miscible with water, in all proportions.

(7) (a) To four drops of the liquid dried over potassium carbonate in a test-tube added a clean bit of sodium. There was a vigorous reaction in the cold and hydrogen was given off.

(b) Added a few granules of phosphorus pentachloride to three drops of the liquid. There was a vigorous reaction with evolution of hydrogen chloride.

(c) Formation of an ester was noticed when a few drops of the liquid were heated with acetic anhydride and poured into dilute sodium carbonate solution.

The above tests showed that the substance was an alcohol.

(8) The liquid gave the iodoform reaction *even in the cold*.

(9) *Examination of the products of oxidation.* In a small distilling flask of 25 c.c. capacity 6-7 c.c. of chromic acid mixture were taken and 2 c.c. of the alcohol added drop by drop. There was a vigorous reaction even in the cold. After the reaction sub-



sided, the contents of the flask were gently heated and the distillate collected in a test-tube surrounded by cold water. 3 c.c. of the distillate were obtained. The distillate was tested as follows :—

- (a) with Fuchsin aldehyde reagent—no reaction.
- (b) with Tollen's reagent—slight reduction.
- (c) Fehling's solution—no reduction.
- (d) with Borsche's reagent—orange yellow needle-shaped crystals melting at 126-127° were obtained.

The oxidation product is therefore a ketone and from the melting point of the 2:4-dinitrophenylhydrazone it was inferred that acetone was the oxidation product.

(e) with sodium nitroprusside solution (1%) the reaction given was identical with that for acetone.

#### **Confirmatory test for acetone**

0.5 c.c. of the distillate and 1 c.c. of benzaldehyde were dissolved in 4 c.c. of absolute alcohol and boiled for a few minutes after adding 1 c.c. of 2N sodium hydroxide. When the solution was cooled, crystals of the dibenzylidene acetone separated. After recrystallisation from alcohol the melting point of the crystals was found to be 110°. (Dibenzylidene acetone, m.p. 111°-112°.)

Hence the original substance was ISOPROPYL ALCOHOL (b.p. 83°). Its isomer n-propyl alcohol boils at 97° and does not give the iodoform reaction. The 3 : 5-dinitrobenzoate of the original alcohol was prepared and recrystallised from rectified spirits. The compound melted at 121°.

Isopropyl ester of 3:5-dinitrobenzoic acid melts at 122°.

### **Substance 3**

A colourless liquid with a fragrant odour, insoluble in water (b.p. 214°).

#### **Detection of elements**

Nitrogen, sulphur and halogens are absent.

#### **Preliminary reactions**

- (1) An aqueous solution of the liquid was neutral to litmus.
- (2) Sodium hydroxide and sodium bicarbonate did not react with the substance in the cold ; but a few drops of the liquid on boiling with a solution of sodium hydroxide, slowly dissolved. There was however no evolution of ammonia.
- (3) When heated with sulphuric acid, it dissolved with slight carbonisation.

**Classification reactions**

(4) The liquid did not answer the tests for aldehydes or acids.

(5) On adding a bit of clean sodium to a few drops of the given liquid, a solid substance separated but no hydrogen was found to be given off.

The given liquid might therefore be an ester.

(6) 2 c.c. of the liquid was treated with 10 c.c. of 10% alkali in a round-bottom flask fitted with a reflux condenser and refluxed for about an hour. The smell of the ester had disappeared. Distilled the contents till about half the liquid distilled over. Reserved the distillate for testing the alcohol.

On acidifying a little of the residue (the sodium salt) with dilute sulphuric acid, no precipitate was obtained. Probably the acid belonged to the class of acids soluble in water.

*Test for the alcohol*

(a) With a few drops of the alcohol carried out the iodoform reaction. Formation of iodoform was noticed.

(b) Saturated the remainder of the distillate with solid potassium carbonate and there was a separation of the alcohol which was removed by means of a pipette. The volume of alcohol so obtained was about 0.5 c.c. With this quantity prepared the *p*-nitrobenzoyl derivative by heating gently with about 0.3 g. of the acid chloride, then diluting with water and finally washing with sodium carbonate solution. The solid derivative, after recrystallisation, melted at 58° (m.p. of ethyl *p*-nitrobenzoate 57-58°).

Hence the alcohol is ethyl alcohol.

(7) *Hydrolysis with sulphuric acid.* 2 c.c. of the ester was treated with 5 c.c. of sulphuric acid diluted with its own volume of water in a 6" × 1" test-tube fitted with a one-holed cork and a long condenser tube and kept gently boiling for about 20 minutes. On cooling, a solid acid was obtained. Diluted the contents of the tube with 5 c.c. of water and filtered the solid acid. Washed the acid with ice-water. The acid melted at 183°.

(a) Heated a small amount of it in a test-tube. The acid melted to a clear liquid and a little later a white sublimate (probably of an anhydride) was obtained.

(b) To a little of the solution of the neutral salt (prepared by dissolving the acid in a slight excess of ammonia and boiling off the excess of ammonia), added ferric chloride solution. A reddish

precipitate of the ferric salt was obtained insoluble in acetic acid, but dissolving in dilute hydrochloric acid without any precipitation of the free acid (Cf. benzoic acid).

(c) Heated a little of the acid with a little resorcinol and a drop of concentrated sulphuric acid. A reddish solution was obtained, and on pouring into sodium hydroxide a bright green fluorescence was obtained. This reaction suggested the presence of either succinic or phthalic acid but the melting point pointed to the presence of the former acid.

(d) *Preparation of a derivative.* With about 0.1 g. of the acid the p-toluidide was prepared as usual and recrystallised from alcohol. After drying, the crystals melted at  $252^{\circ}$ .

The melting point of succin-p-toluidide is  $255^{\circ}$ .

Hence the acid was succinic acid and the ester therefore was DIETHYL SUCCINATE, (b.p.  $216^{\circ}$ ).

#### Substance 4

A white crystalline substance insoluble in water, (m.p.  $48^{\circ}$ ).

(1) A small amount of the substance, when heated on a crucible lid, burnt away with a smoky flame leaving no residue. Hence the substance was aromatic and no metallic constituent was present.

(2) **Detection of elements.** Nitrogen, sulphur and halogens were absent.

(3) **Preliminary reactions.** (a) Aqueous or alcoholic solution had no action on litmus.

(b) Warm concentrated sulphuric acid alone dissolved the substance with formation of a yellow solution.

(c) With cold alkaline permanganate there was oxidation.

(4) **Systematic examination** for substances containing carbon, hydrogen and oxygen.

(a) Since the substance was insoluble in water, a small amount was dissolved in a little alcohol and treated with Schiff's reagent. No coloration was noticed.

(b) Molisch's test for carbohydrates was not answered.

(c) A small amount of the substance (0.1 g.) was dissolved in a little alcohol, 1 c.c. of the hydroxylamine hydrochloride reagent was added and then 2 c.c. of alcoholic potash. The mixture was heated for about five minutes to boiling, then diluted with water, acidified with acetic acid and shaken. A white solid oxime soon separated showing that there was a carbonyl group present.

(d) The substance did not reduce Fehling's solution nor was there reduction with Tollen's reagent.

Hence a ketone was indicated.

The precipitated oxime was recrystallised from alcohol and melted at  $142^{\circ}$ . The oxime of benzophenone melts at  $141^{\circ}$ .

(e) **Confirmatory test.** As a confirmatory test the 2 : 4-dinitrophenylhydrazone of the substance was prepared and the melting point of the derivative was found to be  $231^{\circ}$ .

The m.p. of the 2 : 4-dinitrophenylhydrazone of benzophenone is  $229^{\circ}$ .

Hence the original substance was BENZOPHENONE.

### Substance 5

A colourless liquid insoluble in water (b.p.  $154-156^{\circ}$ ).

(1) A drop of the liquid was introduced into the Bunsen flame at the tip of a glass rod. The liquid burnt with a highly smoky flame indicating that it was rich in carbon.

(2) **Test for elements.** Nitrogen and sulphur were absent. Halogen was present. The halogen was identified as bromine.

(3) **Preliminary reactions.** (a) Moist litmus was unaffected.

(b) Two drops of the liquid were boiled with sodium hydroxide solution. There was no perceptible change. The liquid was cooled, acidified with nitric acid, treated with silver nitrate and heated. No precipitate was obtained. The halogen was therefore in the nucleus.

(c) Alcoholic silver nitrate was unaffected, when a few drops of the liquid were warmed with it.

(d) 0.5 c.c. of alkaline permanganate was added to three drops of the liquid and boiled for a few minutes. The permanganate was not decolorised.

From the above experiments it is evident that the compound is aromatic with the halogen attached to the ring and that there is no side-chain.

(e) Two drops of the liquid were added to 0.5 c.c. of concentrated sulphuric acid and gently heated. The liquid dissolved and on diluting with water, showed no signs of separation. Hence the tendency of the substance to get sulphonated like hydrocarbons was indicated.

This behaviour is characteristic of ring-substituted halogen hydrocarbons which resemble closely the parent hydrocarbons in most respects.

(f) 2 c.c. of concentrated sulphuric acid were added to 1 c.c. of concentrated nitric acid, the acid mixture was cooled in ice and to this 10 drops of the liquid were added drop by drop with frequent shaking. The liquid slowly dissolved and after about 10 minutes a pale yellow solid separated. The liquid was diluted with 3-4 c.c. of water and the precipitate filtered and crystallised from boiling alcohol when it separated in light yellow needle-shaped crystals melting at  $125^{\circ}$ . p-Nitrobromobenzene melts at  $126^{\circ}$ .

(g) To a mixture of 2 c.c. of concentrated nitric and 2 c.c. of sulphuric acid, 10 drops of the liquid were added and heated gently on a flame. The liquid easily dissolved and after heating on a boiling water-bath for about 15 minutes, the liquid was cooled and diluted with water. A yellow oil separated which, on cooling and rubbing vigorously, solidified. The yellow solid was filtered and crystallised from alcohol. The crystals melted at  $74^{\circ}$ . 2 : 4-Dinitrobromobenzene melts at  $75^{\circ}$ .

(h) Ten drops of the liquid were added to 1 c.c. of fuming sulphuric acid (10%  $\text{SO}_3$ ), the mixture shaken after each addition, and cooled under the tap to prevent undue heating. After keeping for about ten minutes, the mixture was diluted with 5 c.c. of water, 3 g. of powdered sodium chloride were added and the mixture warmed on the water-bath till the sodium chloride dissolved. On cooling, the sodium salt of p-bromobenzenesulphonic acid slowly crystallised out. This was filtered and dried.

The dry sodium salt was converted into the sulphonyl chloride as described under o-xylene (*vide* derivatives). The sulphonyl chloride after crystallisation from ligroin melted at  $74^{\circ}$ .

The sulphonyl chloride was evaporated with a slight excess of concentrated ammonia. The sulphonamide separated, and on crystallisation from alcohol, formed fine colourless needles, melting at  $161^{\circ}$ . p-Bromobenzenesulphonamide melts at  $160^{\circ}$ .

Hence the original liquid was BROMOBENZENE (b.p.  $157^{\circ}$ ).

### Substance 6

A light yellow coloured liquid (b.p.  $204\text{--}206^{\circ}$ ).

(1) A drop of the liquid was introduced at the tip of a glass rod into the Bunsen flame. It burned with a highly smoky flame.

(2) **Detection of elements.** The liquid contained nitrogen, was not soluble in water and had an aniline-like odour. The aqueous solution had no action on litmus.

(3) **Preliminary reaction.** (a) The substance did not dissolve either in sodium carbonate or sodium hydroxide.

(b) To a few drops of the substance dilute hydrochloric acid was added and the mixture shaken. The liquid dissolved and on adding sodium hydroxide solution, separated again as an oil. Hence it might be an amine.

(c) **Test for primary amine.** The carbylamine test was not answered.

**Tests for secondary amine.** (1) 3 drops of the substance were dissolved in dilute hydrochloric acid, and sodium nitrite was added drop by drop till a slight excess was present. A yellow oil separated which was extracted with ether. After evaporation of the ether, the yellow oil was treated with a little phenol and concentrated sulphuric acid. The characteristic Liebermann's reaction was noticed.

(2) Simon's reaction for secondary amines was also answered by the substance.

Hence the substance was a secondary amine.

*Preparation of derivative.* To 3 drops of the amine an equal amount of concentrated hydrochloric acid was added. The mixture was shaken and cooled in ice. The solid hydrochloride which separated was transferred directly to a porous plate, pressed well with a spatula and its melting point determined. It melted at  $174^{\circ}$ . The melting point of the hydrochloride of ethyl aniline is  $176^{\circ}$ .

Hence the original liquid was probably ETHYL ANILINE.

### Substance 7

A pale yellow liquid, with the smell of bitter almonds, insoluble in water (b.p.  $217-218^{\circ}$ ).

(1) A drop of the liquid introduced at the tip of a glass rod into the Bunsen flame burnt with a highly smoky flame showing richness in carbon.

(2) **Elements present.** The substance contained nitrogen without sulphur or halogens.

(3) **Preliminary reactions.** (a) The liquid was neutral to litmus and did not dissolve in sodium carbonate solution.

(b) It was also insoluble in dilute or concentrated hydrochloric acid.

(c) It was unaffected by sodium hydroxide solution either in the cold or even after boiling.

(d) No reaction was observed on boiling with 50 per cent sulphuric acid.

Hence the possibility of the substance being an amine, amide or nitrile is excluded. The only other possibility is its being an aromatic nitrocompound and this is confirmed by reaction (e).

(e) Mulliken and Barker's reaction for the presence of a nitro group was answered.

(f) On boiling a few drops of the liquid with 1 c.c. of alkaline permanganate, decolourisation took place rather slowly.

In all probability a side-chain is present. A reference to literature pointed to the possibility of its being *o*-nitrotoluene (b.p. 220°). This was confirmed by the preparation of the following derivatives :

2 : 4-*Dinitrotoluene*. Using 5 drops of the liquid, the nitration was carried out exactly as described (on p. 52) but in warm solution. The solid which was obtained melted after recrystallisation from alcohol at 71° (m.p. of 2 : 4-dinitrotoluene, 70°).

**Reduction to the corresponding amine.** 0.5 c.c. of the liquid was reduced with tin foil and concentrated hydrochloric acid as usual and excess of 15 per cent sodium hydroxide sufficient to dissolve the stannic hydroxide and liberate the amine was added. The amine was benzoylated by the Schotten-Baumann method and the benzoyl derivative, after recrystallisation from dilute alcohol, melted at 142° (m.p. of benzoyl-*o*-toluidide, 143°).

**Oxidation.** Oxidation of the nitro compound with alkaline permanganate to the corresponding nitrobenzoic acid was carried out as usual. The nitrobenzoic acid melted at 148°. *O*-nitrobenzoic acid melts at 148°.

Hence the substance was *O*-NITROTOLUENE.

### Substance 8

A colourless crystalline substance, partly liquid, boiling at 200°, slightly soluble in water, with a phenolic odour.

**Preliminary reactions.** (1) Easily burned with a sooty flame.

(2) **Elements.** Nitrogen, sulphur and halogens were absent so that the substance had to be looked for under compounds containing carbon, hydrogen and oxygen.

(3) The aqueous solution had a slight acid reaction, but did not dissolve in sodium carbonate or in bicarbonate solution.

(4) On shaking 6 drops of the liquid with 3 c.c. of sodium hydroxide (2N) it dissolved readily forming a clear solution which was not affected by exposure to air. On saturating the solution with carbon dioxide, the original oily drops were re-formed.

(5) 2 drops of the liquid were shaken with 1 c.c. of water and to the aqueous solution a few drops of neutral ferric chloride solution were added. A blue colour discharged by dilute mineral acids was observed.

(6) Phthalein fusion carried out as on p. 66 gave a red colour in the presence of alkali.

(7) A slight reducing action with silver nitrate solution was noticed.

From the results of the reactions cited above, the phenolic nature of the compound is evident. The formation of blue colour with ferric chloride and the absence of any marked reducing property indicate one of the cresols, meta or para. Choice between the two alternatives was arrived at on the basis of the following evidence.

(1) The given substance did not form a picrate by the usual methods.

(2) The benzoyl derivative prepared as usual, melted at  $71^{\circ}$  (m.p. of the benzoyl derivative of p-cresol is  $71^{\circ}$  whereas that of m-cresol is  $54^{\circ}$ ).

(3) Carboxymethyl ether of the phenolic compound melted at  $136^{\circ}$ .

Hence the substance was P-CRESOL.

### Substance 9

A white crystalline substance, soluble in water. It did not melt at all.

(1) **Preliminary reactions.** On heating 0.3 g. of the substance in a porcelain crucible, it charred and finally a white residue was left behind.

(2) **Test for elements.** Sulphur was present and examination of the residue from (1) showed that it contained sodium. The



residue was dissolved in water, and to a part dilute hydrochloric acid was added. Sulphur dioxide as well as hydrogen sulphide were given off. A second part answered the test for a sulphate.

Hence the substance might be the sodium salt of a sulphonic acid.

(3) From the sodium salt, the sulphonyl chloride was prepared as usual and from the sulphonyl chloride, the sulphonamide was obtained. These after recrystallisation melted at  $69^{\circ}$  and  $136^{\circ}$  respectively. The melting points of p-toluenesulphonylchloride and p-toluenesulphonamide are  $69^{\circ}$  and  $137^{\circ}$  respectively.

(4) **Alkali fusion.** For further confirmation the phenol was obtained by fusing 4 g. of caustic potash (which is preferable to caustic soda) and 1 g. of the sodium salt with a little water in a nickel crucible till there was complete decomposition and the potassium salt of the phenol was seen floating like an oily layer. The melt when cold was extracted with hot water and a part of the strongly alkaline solution was benzoylated as usual. The benzoyl derivative melted at  $71^{\circ}$ .

A second portion of the melt was carefully neutralised with dilute hydrochloric acid and treated with ferric chloride. A bluish green colour was noticed.

Hence the phenol was p-cresol.

The original substance was therefore SODIUM PARA-TOLUENE SULPHONATE.

### Substance 10

A white amorphous substance soluble in water decomposing at about  $203^{\circ}$ .

(1) A small amount of the substance heated on a piece of porcelain charred and left no residue on stronger heating.

(2) **Elements.** The substance did not contain nitrogen or the other elements.

(3) **Preliminary reactions.** (a) Aqueous solution was neutral to litmus.

(b) It was unaffected by sodium hydroxide solution in the cold. The solution became yellow and finally brown on prolonged boiling.

(c) Cold concentrated sulphuric acid produced no effect but on placing in a boiling water-bath, charring took place.

(4) **Systematic tests.** (a) Molisch's test for carbohydrates was answered.

(b) Fehling's solution as well as Tollen's reagent were reduced.

(c) Barfoed's reagent was not reduced. Hence the substance was probably not a monosaccharide.

(d) Preparation of the osazone by the usual methods showed that the osazone was obtainable only after a long time and on cooling. The osazone obtained after recrystallisation (m.p.  $200^{\circ}$ ) was observed under the microscope and found to possess the characteristics of lactosazone.

**Mucic acid test.** Oxidation of 0.5 g. of the sugar yielded the insoluble mucic acid.

These results lead to the conclusion that the substance is LACTOSE.

### Substance 11

A light coloured crystalline substance slightly soluble in water, melting at  $80^{\circ}$ .

(1) **Odour.** The substance possessed a pleasant vanilla like odour.

(2) **Elements.** Nitrogen, halogens and sulphur were absent. The substance completely burnt away leaving no residuc.

(3) **Preliminary reactions.** (a) Aqueous solution was neutral to litmus. Substance did not dissolve in sodium carbonate with effervescence. Hence, no carboxyl group was present.

(b) It dissolved readily in dilute sodium hydroxide solution. The solution did not darken and the original substance was only partly reprecipitated on passing carbon dioxide.

Neutral ferric chloride gave with an alcoholic solution of the substance a characteristic blue colour. Hence a phenolic group was present.

(c) No characteristic reaction was observed when the substance was heated with concentrated sulphuric acid, excepting that the solution became reddish.

(d) The substance decolourised cold permanganate showing the presence of either an easily oxidisable compound or an aldehydic group.

(e) Action of bromine in glacial acetic acid showed absence of unsaturation. Plenty of hydrogen bromide was evolved showing substitution.

(4) **Systematic tests.** (a) Alcoholic solution of the substance had no action on Schiff's reagent. Neither Fehling's solution nor ammoniacal silver nitrate was reduced.

(b) The substance readily condensed with semicarbazide, phenylhydrazine and hydroxylamine yielding a semicarbazone, phenylhydrazone and an oxime. These reactions pointed to the existence of a carbonyl group. The ready oxidisability pointed to an aldehyde group being present. The acid, however, was difficult to isolate.

(c) Decomposition with hydriodic acid showed the presence of a methoxy group.

(5) **Confirmatory tests by preparation of derivatives.**

*Tests for phenolic group.* Preparation of acetyl derivative : The substance was dissolved in the minimum amount of alkali, acetic anhydride added and shaken, keeping the solution alkaline. The acetyl derivative that was precipitated was recrystallised from alcohol and its m.p. was found to be  $87^{\circ}$ .

*Tests for carbonyl group.* The semicarbazone was prepared as usual. It was obtained as a white crystalline precipitate sparingly soluble in alcohol, and after crystallisation, melted at  $230^{\circ}$  (correct m.p.  $229^{\circ}$ ).

The oxime was obtained by warming on a water-bath a dilute alcoholic solution of the substance with hydroxylamine hydrochloride and sodium acetate. The mixture was evaporated to dryness and the oxime extracted by ether. The oxime recovered melted at  $118^{\circ}$  (correct m.p.  $117^{\circ}$ ).

From these reactions it was evident that it contained a phenolic hydroxy group, a methoxy group, and an aldehyde group. From the melting points of the substance and of its derivatives and from its characteristic odour the substance was proved to be Vanillin.

## CHAPTER VIII

### ANALYSIS OF MIXTURES

While in inorganic qualitative analysis it is easy through well-defined group separations to identify the metallic radicals of a given mixture without a preliminary separation of the component salts, the identification of the components of a mixture of organic substances without separating them is an almost impossible task. The difficulty is enhanced by the fact that a substance can possess two or more groups which function independently of each other. It is possible, however, to effect a separation of the constituents on the basis of (a) differences in physical properties such as the boiling point in the case of liquids, solubility in different solvents in the case of solids, or even volatility, and (b) of differences in chemical behaviour towards acids, dilute or concentrated alkaline saturated bisulphite solution, acetylating reagents, etc. Greater prominence should be given to chemical methods and it is only when they fail that physical methods which are often rather laborious should be applied.

#### **Division and classification of substances**

For the purpose of chemical examination substances may be grouped into :

(a) *Acidic substances*, such as carboxylic acids, sulphonic acids, phenols and somewhat rarely imides.

(b) *Basic substances*, such as amines or amino compounds or cyclic bases and their derivatives ;

(c) *Neutral substances*. Under this group we have a large class of compounds, both reactive and non-reactive. Among the reactive compounds are to be included alcohols, aldehydes, ketones, esters, carbohydrates, aliphatic halogen compounds, etc. Among the non-reactive compounds are the hydrocarbons, ethers, aliphatic as well as phenolic, aromatic hydrocarbons with halogen in the nucleus, aromatic nitrocompounds, etc.

A preliminary examination should precede the separation and should be carried out on the same lines as those outlined for the identification of simple substances. About one-sixth of the given quantity (1-2 g.) should be reserved for this purpose, and from the conclusions of the preliminary examination a quanti-

tative separation should be attempted. The preliminary examination consists of :—

- (a) noticing any peculiar colour, or odour ;
- (b) an ignition test to find any inorganic material from salts of acids carboxylic or sulphonic ;
- (c) testing for elements ;
- (d) solubility behaviour : Portions of mixture (0.1 g.) should be treated in a small test-tube with (1) water and (2) ether. Enough solvent should be added so as to make sure that the amount present is not insufficient. The mixture is shaken well noticing whether a part or the whole of the mixture has completely dissolved. In cases of doubt a portion of the clear solution is withdrawn by a suction pipette and the solution evaporated on a watch glass to see if a part of the mixture has gone into solution.

In the case of liquid mixtures, a contraction in volume, on adding water usually indicates the solubility of a component in water.

Thus it can be found out whether the given mixture is completely soluble in water or ether, or partly soluble in either.

Mixtures given for analysis are either solids or liquids, the latter being made up of liquid components or of a solution of solids in liquids. They usually admit of being separated into their constituents on the basis of differences in physical or chemical properties.

### **Preliminary reactions**

(1) Test aqueous solution with litmus to see if it is acidic or basic.

(2) To portions of the mixture add separately in different test-tubes the following reagents and shake well, warming if necessary :

(a) Dilute hydrochloric or sulphuric acid. If only a part is soluble, one of the constituents is basic. If the mixture is entirely soluble in acid *it is likely* that both the constituents are basic.

(b) *Concentrated sulphuric acid.* If one of the constituents dissolves slowly on warming without charring, a hydrocarbon or even an ether may be inferred but if decomposition is noticed no definite inference can be drawn. If on dilution with ice-cold water, the original substance is liberated, an ether may be confirmed.

(c) *Aqueous sodium bicarbonate.* Vigorous effervescence followed by solution indicates the presence of an acidic constituent. On acidifying, the clear liquid liberates the acid, if insoluble.

(d) *Aqueous potash.* If one or both the constituents dissolve in the cold, a phenol or an acid or a mixture of both may be inferred. The solution is filtered and saturated with carbon dioxide. A phenol, whether solid or liquid, is usually reprecipitated.

(e) *Alcoholic potash.* Reflux for about 5 minutes a small amount of the mixture in a test-tube with 3 c.c. of alcoholic potash and dilute with water to see if any constituent has disappeared. If ammonia is evolved during this operation an amide or imide may be inferred. This inference should tally with the test for nitrogen. In the absence of nitrogen, an ester is indicated.

(f) *Reaction with ferric chloride.* A purple colour often indicates an ortho-hydroxy compound or a simple phenol or ketonic ester like ethyl aceto-acetate in its enolic form.

The reactions if any are indicative of phenols in general or hydroxy acids, if in addition test (1) is answered.

(g) Treatment with bromine in carbon bisulphide or with dilute permanganate. If decolourisation takes place, unsaturation is indicated.

### **Separation of ether soluble mixtures**

On the basis of the foregoing reactions a more or less quantitative separation is attempted. The rest of the mixture is weighed and shaken up in a separating funnel with sufficient *dry* ether to dissolve the whole of it. The ether extract may be filtered to free it from mechanical impurities, returned to the separating funnel and shaken successively twice with 10 c.c. of the following reagents :

(1) *Dilute sulphuric or hydrochloric acid* to remove any basic component which will be possible only if nitrogen is present. This extract is separated and rendered alkaline to liberate the free base which is recovered by extraction with ether again.

(2) *Bicarbonate solution.* The ether solution is washed with water and then shaken with sodium bicarbonate solution. Nitrophenols and carboxylic acids are removed. The sodium carbonate extract on acidifying, sets free the acids which are precipitated, if insoluble, while soluble acids can be recovered only by extraction with some suitable solvent.

Nitrophenols colour the solution strongly and may be detected at once.

(3) *Dilute caustic soda.* The ether solution is next extracted with dilute (2N) sodium hydroxide solution. The object is to remove phenols or naphthols which are too feebly acidic to be removed by the carbonate. The sodium hydroxide extract on saturation with carbondioxide or on acidifying, liberates the phenols as oils or solids which are recovered by extraction with ether in a pure state for further examination.

The presence or absence of basic and acidic constituents having been established as above, the ether extract now contains neutral compounds such as aldehydes, ketones, esters, alcohols, hydrocarbons, ethers and miscellaneous compounds.

The ether extract is now shaken up with a freshly prepared solution of saturated sodium bisulphite. If a precipitate of the bisulphite compound is obtained it is filtered and treated with sodium carbonate or a dilute acid to liberate the aldehyde or ketone. All aldehydes and ketones do not form bisulphite compounds equally readily.

The further separation of the mixture depends on the knowledge gained about the nature of the components present. The ether may be removed at this stage and the components if solid are separated by fractional crystallisation or by fractional distillation if they are liquids, in other words by physical methods. In effecting a separation by steam distillation which is somewhat rarely applied, it is essential to know that the component which is non-volatile is not decomposed by steam.

In the case of a mixture of an ester with a hydrocarbon or an ether or a ketone, where the boiling points of the components lie close together and fractional distillation does not help in the separation, fractional hydrolysis is sometimes applied. When a liquid mixture is made up of members of a homologous series, fractional distillation is the only method available and is applied using a short and efficient fractionating column.

### **Analysis of the components**

The separated components are purified by the usual methods and the test for elements should be made with the dry substances, as it is quite possible that both the constituents contain some elements in common. The purity is to be established by a melting point determination if solid and a boiling point determination if

liquid. Further procedure is the same as that outlined already (Chapter V) for simple substances.

### **Water-soluble mixtures**

There is only a limited number of mixtures that can be made up where both the constituents are soluble in water. Compounds coming under this category are the lower aliphatic alcohols, aldehydes, ketones, acids and their sodium or potassium salts, the simple sugars, salts of aliphatic and aromatic bases as well as salts of sulphonic acids.

The procedure for examination is more or less the same as that outlined for ether soluble mixtures. A portion is reserved for a preliminary examination. The following tests are applied.

- (a) Action of litmus on aqueous solution ;
- (b) Ignition test and examination for inorganic basic radicals with the residue, if any, left behind on strong ignition ;
- (c) Test for elements with the original mixture, which should not contain water, as testing for elements with aqueous solution is dangerous.

(d) Action of dilute hydrochloric acid if the original mixture is basic in reaction. Liberation of any insoluble acid from its sodium salt may take place.

(e) Action of dilute sodium hydroxide. Changes in colour, evolution of gases such as lower aliphatic amines, or even ammonia from amides, liberation of oily bases from aromatic, amines salts, etc., should be carefully observed.

An ether extraction may be made to see if ether soluble substances are liberated during this test.

(f) Distillation with dilute sulphuric acid or phosphoric acid. A small portion of the mixture (0.5 g.) is distilled with dilute sulphuric acid in the small distilling apparatus and volatile acids, if any, such as formic, acetic, etc., from the salts of lower fatty acids are absorbed in water and the distillate tested for such acids.

(g) A similar distillation with sodium hydroxide solution is made and the distillate examined for volatile bases.

(h) A simple distillation without the addition of acid or alkali can also be made and the products tested for neutral substances such as alcohols, ketones, aldehydes, etc.

Neutral substances like alcohols and ketones can be separated from their aqueous solutions by saturating with solid potassium carbonate.



Tests, like the iodoform test, and the routine tests for aldehydes, ketones, etc. should be applied both with the original mixture and the various distillation fractions. Even if separation is not possible the individuals can be recognized by the above tests.

### **Mixtures which are partly soluble in water or ether**

The method of examination consists in separating the mixture into water-soluble and ether-soluble constituents ; by repeated extraction with small amounts of water or ether and examining each part as already outlined.

### **Typical analyses of some simple mixtures containing two substances**

#### **Mixture 1**

A light coloured homogeneous solid weighing nearly 10 g.

No characteristic odour was noticeable.

Ignition of a small amount (0.05 g.) left no residue showing the absence of any inorganic constituent.

#### **Detection of elements**

Test for elements did not reveal the presence of nitrogen, halogen or sulphur.

*Solubility tests.* (1) 0.1 g. of the mixture was shaken with 1 c.c. of water in a small test tube. The mixture did not dissolve much in the cold solvent but on heating, it dissolved completely and crystallised out on cooling. No appreciable difference in the solubility of the constituents could be noticed. The solution was acidic to litmus.

(2) When the experiment was repeated with ether, the mixture was found to dissolve completely.

Action of dilute hydrochloric or concentrated sulphuric acid did not reveal any characteristic changes. Since nitrogen was absent the possibility of a basic constituent was excluded.

*Action of sodium carbonate.* 0.1 g. of the mixture was treated with 1-2 c.c. of dilute sodium carbonate solution and stirred for a few minutes. A part of the mixture dissolved and the clear solution after removal by a suction pipette and cautiously acidifying with dilute hydrochloric acid threw down a precipitate. Hence the presence of an acid was confirmed.

*Aqueous potash.* The mixture dissolved completely in alkali. The solution on saturation with carbon dioxide gave a precipitate showing that a phenol was probably present.

*Reaction with ferric chloride.* An aqueous solution of the mixture gave with neutral ferric chloride a somewhat purple colour.

Since the presence of an acid and a phenol was thus established the rest of the mixture weighing about 8 g. was shaken up with dry ether (20 c.c.) in a separating funnel and shaken twice or thrice with sodium carbonate solution in lots of 5 c.c. each till all the acid was extracted out (test). The solution of the sodium salt was concentrated to half the bulk, acidified, the precipitated acid was filtered and recrystallised from water and the weight of the dry acid was obtained (3.5 g.).

Evaporation of the ether solution furnished the phenol which was also purified by crystallisation.

### Examination of the acidic constituent

(1) Aqueous solution of the acid gave a purple colour with neutral ferric chloride solution.

(2) On heating with soda-lime, phenol was obtained.

Proceeding in the manner outlined for the analysis of simple substances the acid was identified as *salicylic acid*.

*Derivative prepared.* 5-Nitrosalicylic acid (m.p. 226°). The phenol was identified as *β-naphthol*.

*Derivatives prepared.* (1) *β*-Naphthyl methyl ether (m.p. 72°).

(2) *β*-Naphthyl acetate (m.p. 70°).

### Mixture 2

A light brown homogeneous liquid weighing nearly 10 g.

A characteristic odour resembling that of aromatic amines was noticed.

A drop of the mixture introduced into the Bunsen flame burnt with a smoky flame showing richness of carbon content.

Test for elements showed the presence of nitrogen only.

### Solubility tests

The mixture dissolved completely in ether and was insoluble in water.

The mixture dissolved completely in dilute hydrochloric acid. No characteristic changes were observed with concentrated sulphuric acid.

Since the mixture did not react with sodium hydroxide or carbonate or ferric chloride, an acid or a phenol was inferred to be absent. Carbylamine reaction was not answered. Hence the mixture did not contain a primary amine. A small amount of the mixture, 0.5 g., was shaken up with ether and the ether solution treated with dilute hydrochloric acid twice and shaken in the small separating funnel. After this treatment the ether extract left no residue on evaporation, while the acid extract on making alkaline, became turbid and oily drops separated. This behaviour pointed to the presence of two amines. Separation by fractional distillation was not possible as the mixture distilled over completely at 192-195°.

Reaction with sodium nitrite solution in the cold gave a crystalline orange precipitate, together with a greenish oil. Extraction with ether removed the oil while the orange crystalline precipitate did not disappear. Evaporation of the ether furnished two to three drops of a yellowish green oil which answered the Liebermann's test. Hence the presence of a secondary aromatic amine was indicated. The other constituent might probably be a tertiary amine.

The mixture weighing 8 g. was treated with an equal amount of acetic anhydride in a 100 c.c. round-bottom flask carrying an air condenser and heated to boiling for about 10 minutes. The mixture was cooled and poured into 30 c.c. of water to which 5 c.c. of dilute hydrochloric acid was added. The liquid was then extracted thrice with ether. The ether extract was dried over calcium chloride, and evaporated when the acetyl derivative of the amine was obtained. A little of this after recrystallisation from hot water melted at 101°. The rest of it weighing nearly 3.5 g. was hydrolysed with concentrated hydrochloric acid and the free base recovered after hydrolysis. It boiled at 193°.

Further analysis proved the secondary base to be *methyl aniline*.

*Derivatives prepared.* Benzenesulphonyl derivative, m.p. 78°.

The aqueous extract on adding alkali liberated the base which was extracted with ether and obtained in the free condition boiling at 192-193°. Amount recovered was 3.5 g.

Further analysis proved the base to be *dimethylaniline*.

*Derivative prepared.* p-Nitrosodimethylaniline, m.p. 85°.

Hence the given mixture contained methylaniline and dimethylaniline.

### Mixture 3

A light yellow homogeneous liquid.

The mixture had the odour of bitter almonds.

A drop of it introduced into the burner, burnt with a highly sooty flame.

Test for elements showed the presence of nitrogen only.

### Solubility tests

(1) The mixture was completely soluble in ether and insoluble in water.

(2) The aqueous solution was very faintly acidic.

There was no action with dilute hydrochloric acid, the mixture showing no tendency to dissolve in it.

With sodium carbonate or aqueous alkali or ferric chloride solution there was no reaction.

When treated with Schiff's reagent, a pink colour developed slowly in aqueous solution but much more quickly in dilute alcoholic solution. This pointed to the presence of an aldehyde.

Fehling's solution was not reduced but ammoniacal silver nitrate was reduced. An aromatic aldehyde was probably present.

### Separation of the mixture

The mixture weighing (10 g.) was dissolved in 25 c.c. of ether in a separating funnel and shaken with an equal amount of freshly prepared saturated bisulphite solution. The bisulphite compound that separated was filtered off, and washed with ether to remove the other constituent. The filtrate containing the ether solution of the second constituent was transferred to the separating funnel, the aqueous layer was separated and the ether layer was once again shaken with bisulphite solution to ensure complete extraction of the aldehyde part. The ether layer was washed with water once and then dried over calcium chloride. After removal of ether, the second constituent remained as a yellow liquid which distilled at 205-207°. After distillation its weight was determined (4.5 g.).

*Isolation of the aldehyde.* The bisulphite compound was suspended in a little water in a beaker treated with sufficient dilute sulphuric acid and heated on a water bath till the smell of sulphur dioxide was gone. The aldehyde separated as an oily layer which

was extracted with ether and recovered by distillation. The weight of the aldehyde was roughly 4.5 g. and its boiling point, 197-198°.

The aldehyde portion on testing for elements again, showed the absence of nitrogen.

The second component showed the presence of nitrogen and answered Mulliken and Barker's reaction for a nitro group. Proceeding in the manner outlined for simple substances the separated components were found to be :

(1) **Benzaldehyde**

Derivatives prepared :

- (a) *Benzoic acid*, m.p. 121°
- (b) *Phenylhydrazone*, m.p. 158°
- (c) 2 : 4-*Dinitrophenylhydrazone*, m.p. 234°.

(2) **Nitrobenzene**

(a) *m-Dinitrobenzene*, m.p. 90°

(b) *Acetanilide* : reduction to the amine by tin and HCl and preparation of the acetyl derivative from the amine, m.p. 113°.

**Mixture 4**

A light cream coloured solid.

The mixture had no characteristic smell.

On heating, it charred at first and then burnt away completely leaving no residue, thus showing the absence of any inorganic metallic radical.

Test for elements showed the presence of nitrogen only.

**Solubility tests**

1. The mixture was partly soluble in water, practically insoluble in ether, and partly soluble in boiling alcohol.

2. Aqueous solution was neutral to litmus.

1. The mixture did not dissolve in dilute hydrochloric acid. With sodium carbonate also there was no action.

When boiled with sodium hydroxide solution, ammonia was evolved and at the same time the solution turned brown. Hence an amide or imide was present probably mixed with a carbohydrate or aldehyde.

When treated with concentrated sulphuric acid there was no action in the cold but on warming there was charring.

Schiff's reagent was unaffected.

Barfoed's reagent was reduced as also ammoniacal silver nitrate. Hence a monosaccharide was present.

**Separation of the mixture**

The mixture (8 g.) was treated thrice with cold water in lots of 10 c.c., warmed to 40° and filtered. The residue was washed with water, dried and weighed (4 g.). The solution was evaporated on a water bath. It formed a syrup which did not crystallise readily but solidified only on leaving in a desiccator overnight.

**Insoluble part**

It melted at 232° and contained nitrogen. A portion of the substance was hydrolysed with caustic potash by boiling for about half an hour and the acid isolated. The latter melted at 195° and gave the fluorescein test when heated with resorcinol and a little sulphuric acid.

The anilide of the acid was prepared by heating the original substance with aniline. Plenty of ammonia was evolved and the residue after washing with dilute HCl and recrystallising from alcohol melted at 205°.

The melting point of the original substance was 232° corresponding with that of phthalimide.

**Soluble part**

It contained no nitrogen and gave the tests for a monosaccharide but did not answer Pinoff's test. The osazone was formed very quickly and melted at 205°.

The penta-acetate prepared as usual, melted at 111° (Glucose penta-acetate, m.p. 111°). Hence the mixture contained **Phthalimide** and **Glucose**.

**Mixture 5**

A pale yellow homogeneous liquid.

The mixture had a faint phenolic odour.

It burnt with a highly sooty flame and probably contained substances of aromatic nature.

The elements present were nitrogen and chlorine.

**Solubility tests**

0.5 c.c. of the mixture was shaken up with an equal amount of water. The solubility was not quite appreciable. On adding a few drops of hydrochloric acid, shaking well, siphoning off the clear liquid by a capillary siphon and making alkaline, oily drops

with aniline like odour were formed. The residual liquid insoluble in acids was washed with water and shaken up with dilute sodium hydroxide solution, when a further contraction in volume was noticed. The alkaline solution was siphoned off and rendered acidic. Oily drops with a phenolic odour were liberated. The residue left after shaking up with sodium hydroxide was also an oil and probably the neutral component.

Hence the mixture was composed of a basic, an acidic and a neutral component.

### Separation

Twelve grams of the mixture were dissolved in 25 c.c. of ether in a separating funnel and shaken up first with 10 c.c. of dilute hydrochloric acid. The acid layer was separated and the ether solution was shaken up with another 100 c.c. of acid. The basic part removed by the acid was kept aside for further examination. The ether solution was next washed with a little water and shaken up with sodium hydroxide solution twice. The alkaline extract was similarly kept for further examination. The ether solution containing the neutral component was shaken up with bisulphite solution but nothing was extracted. After washing the ether layer with water, drying over calcium chloride and removing the ether, the neutral component was isolated as an oil distilling at  $132^{\circ}$ .

### Neutral component (4 g.)

1. Contained chlorine.
2. The halogen was in the ring as no precipitate was obtained with alcoholic silver nitrate.
3. The compound did not possess any side chain as no oxidation was possible with permanganate.

Nitration yielded a nitro derivative, m.p.  $52^{\circ}$ , corresponding with 2 : 4-dinitrochlorobenzene. Hence the compound was chlorobenzene.

### Basic constituent

The acid extract was rendered alkaline, saturated with common salt and the base recovered by ether extraction. The amount recovered was 4 g., b.p.  $183^{\circ}$ . Further analysis showed it to be a primary amine.

Derivatives prepared :

Acetyl derivative	...	m.p.	113°
Tribromo „	...	„	118°
Azo $\beta$ -naphthol	...	„	130°

Hence it was aniline.

### Acidic constituent

The alkaline extract was rendered acidic, saturated with salt and the acidic component recovered in the same manner as the basic part. The amount recovered was 3 g ; b.p. 181°.

Derivatives :—Benzoyl derivative	m.p.	67°
Tribromo derivative	m.p.	93°

Hence it was phenol.

The given mixture contained *Aniline*, *Phenol* and *Chlorobenzene*.



## CHAPTER IX

### PREPARATION OF ORGANIC COMPOUNDS

#### Preparation 1

##### ETHYL BROMIDE

Absolute alcohol	... 15 c.c.
Concentrated sulphuric acid	... 11 c.c.
Powdered potassium bromide	... 20 g.

11 c.c. of concentrated sulphuric acid are measured into a 250 c.c. distilling flask and 15 c.c. of alcohol are added drop by drop, cooling the flask under the tap during the addition. Powdered potassium bromide is then added a little at a time and the flask quickly closed by a tight fitting cork. The mixture is distilled by gently heating on a sand-bath, using a Liebig's condenser to the end of which an adapter is attached by means of a cork (Fig. 39)

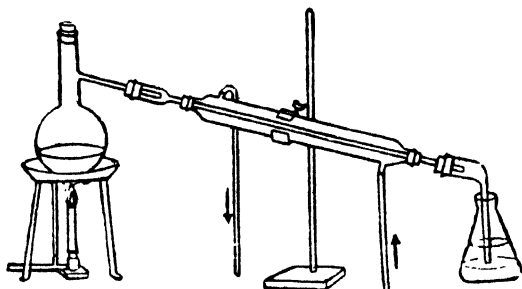
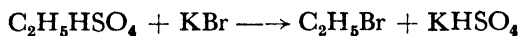
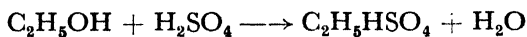


Fig. 39 Preparation of ethyl bromide

The adapter dips into water contained in a conical flask surrounded by ice. A few pieces of washed ice are also introduced into the receiver. Distillation is continued till no more oily drops pass over. If there is any undue tendency for the contents to froth over, the flask is lifted for a moment out of the sand-bath. The ethyl bromide is transferred to a separating funnel (100 c.c.), washed twice with a dilute solution of sodium carbonate (2N) and then thoroughly with cold water. The ethyl bromide which forms the lower layer is dried over calcium chloride for half an hour and distilled by immersion in a hot water-bath (50°) from a distilling flask (30 c.c.) collecting the portion boiling over between

37-39°. It is a colourless liquid, sp. gr. 1.430<sup>20°</sup>, b.p. 38°. Yield, 13 g.

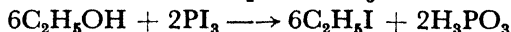
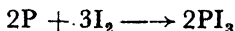


## Preparation 2

### ETHYL IODIDE

Powdered iodine	... 25 g.
Red phosphorus	... 2.5 g.
Alcohol (rectified spirits)	... 13 g. (16 c.c.)

The rectified spirits and the red phosphorus are put into a 100 c.c. round-bottom flask and powdered iodine is added a little at a time while the flask is cooled under the tap. The flask is attached to a reflux condenser plugged loosely at the open end with cotton and left overnight. The contents of the flask are refluxed for about two hours the next morning and the ethyl iodide is then distilled off on a boiling water-bath. The distillate which is usually coloured due to free iodine is transferred to a separating funnel, washed at first with dilute sodium hydroxide (2N) to remove iodine and then with water to remove the alkali. The liquid is dried over anhydrous calcium chloride for about an hour in the separating funnel and redistilled, the portion boiling between 70-74° being collected in a drawn out test-tube and weighed. It is a colourless liquid when freshly distilled; sp. gr. 1.933<sup>20°</sup>, b.p. 72°. Yield, 19 g.



[*Note.* While sealing up the tube, traces of the liquid adhering to the drawn out portion of the test-tube should be removed by filter paper. Otherwise the liquid gets coloured brown with iodine formed as a result of decomposition during sealing.]

## Preparation 3

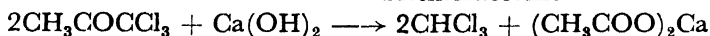
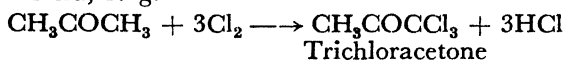
### CHLOROFORM

Bleaching powder	... 100 g.
Water	... 400 c.c.
Acetone	... 25 c.c. (20 g.)

The bleaching powder, freshly prepared, is ground up into a thin cream in a mortar with 300 c.c. of water and transferred after

removing any hard lumps to a 2-litre round-bottom flask fitted with a reflux condenser. The mortar is washed with 100 c.c. of water and the wash liquid also added to the flask. 25 c.c. of acetone diluted with an equal volume of water are added little by little through the condenser with continual shaking. When the vigour of the reaction has subsided, the condenser is removed and the flask is fitted with a one-holed cork carrying a bent tube with the condenser attached for distillation. The flask is heated on a sand-bath and the contents are gently boiled till no more chloroform passes over into the receiver (about  $1\frac{1}{2}$  hours). If there is a tendency for frothing, the flask is lifted temporarily out of the sand-bath. The distillate is transferred to a separating funnel (100 c.c.) with a short stem, washed twice with dilute caustic soda solution (2N) and the lower layer of chloroform is separated. The chloroform is dried for 15 minutes in the separating funnel over granular calcium chloride, a sufficient amount being added to make the liquid clear. The dried liquid is filtered into a dry distilling flask through a cotton plug or folded filter paper and distilled, the distillate passing over between  $60-61^{\circ}$  being collected in a dry test-tube drawn out for sealing up and previously weighed.

It is a colourless liquid with a sweet smell ; sp. gr.  $1.498^{20^{\circ}}$ , b.p.  $61^{\circ}$ . Yield, 15 g.

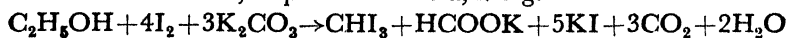


## Preparation 4

### IODOFORM

Alcohol (Rectified spirits)	... 5 g.
Potassium carbonate	... 10 g.
Iodine (powdered)	... 10 g.

The potassium carbonate is dissolved in 40 c.c. of water contained in a 100 c.c. conical flask ; alcohol is added to the solution and then the iodine in small quantities at a time with stirring. The mixture is gradually heated to  $80^{\circ}$  and kept there for about five minutes and then cooled. Iodoform separates in small yellow crystals. It is filtered, washed with water, and re-crystallised from alcohol. It forms lemon yellow crystals with a characteristic odour, m.p.  $119^{\circ}$ . Yield, 2-3 g.



### Preparation 5

#### GLACIAL ACETIC ACID FROM VINEGAR

Vinegar	... 350 c.c.
Sodium carbonate (anhydrous)	... 18 g.

English vinegar contains about 5 per cent of acetic acid. 5 c.c. of the vinegar are titrated against standard sodium hydroxide (N/10) to know the exact acid content. Then 350 c.c. of the vinegar are measured into an 8" porcelain basin and neutralised by adding the calculated quantity of sodium carbonate and the solution evaporated to dryness on a water-bath. The sodium acetate thus obtained is heated on a free flame, when it melts in its water of hydration, then becomes a solid and finally melts again. At this stage it is poured into a clean dry mortar, powdered quickly and cooled in a desiccator. The dry sodium acetate is transferred to a distilling flask after weighing and the quantity of concentrated sulphuric acid required to liberate the acetic acid is calculated. Twice this amount (about 30 c.c.) of sulphuric acid is added slowly while cooling between each addition. The distilling flask is fitted with a thermometer and the acetic acid is distilled, the fraction coming over between 110-120° being collected. This is redistilled after adding a little concentrated sulphuric acid (10 c.c.) the fraction distilling between 117-120° being collected. It is a colourless liquid with a pungent smell, which readily freezes in ice, m.p. 16.7°, b.p. 118°, sp. gr. 1.049<sup>20°</sup>. Yield, 14 g.

### Preparation 6

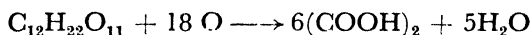
#### OXALIC ACID

Concentrated Nitric Acid	... 200 g. (140 c.c. sp. gr. 1.42).
Cane sugar	... 40 g.

*Note.* (This experiment is to be performed in a fume cupboard.)

The concentrated nitric acid is measured into a 500 c.c. round-bottom flask and the cane sugar added in one lot. The mixture is warmed on a water-bath till the reaction starts, after which it is allowed to proceed without application of heat. The reaction becomes very vigorous at first with evolution of plenty of brown fumes of oxides of nitrogen. At this stage the flask is

cooled in water. After the reaction has ceased the liquid is kept at room temperature for 24 hours, when colourless crystals of oxalic acid are found to have separated. The supernatant liquid is drained off from the crystals and concentrated on a water-bath. A further quantity of oxalic acid separates on cooling. The crystals are filtered on a Hirsch porcelain funnel or an ordinary funnel with a filter disc but without any filter paper and recrystallised from the minimum amount of hot water. It crystallises with two molecules of water (hydrate), mp.  $101.5^{\circ}$ . Yield, 10 g.



[*Note.* An increased yield may be obtained by using vanadium pentoxide (0.1 g.) as catalyst in the oxidation.]

### Preparation 7

#### MUCIC ACID (FROM LACTOSE)

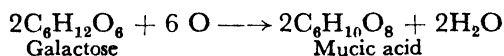
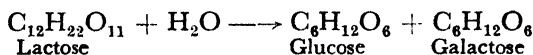
Lactose	... 12 g.
Nitric acid (sp. gr. 1.15)	... 130 c.c.

[Prepared by mixing 37 c.c. of the concentrated acid (sp. gr. 1.42) with 93 c.c. of water.]

The lactose is treated with the nitric acid in a 12 cm. porcelain basin and evaporated over a free flame to a volume of about 25 c.c. A Bunsen burner with a rose-top is most suitable for this purpose and prevents charring. When the mass becomes pasty owing to the separation of mucic acid, the dish is cooled and the contents diluted with 40 c.c. of water. The product is filtered, dried and weighed. The crude mucic acid is purified by adding the acid to cold N/2 sodium hydroxide, the quantity of alkali necessary being roughly calculated from the weight of the crude acid obtained. The solution is decolourised by adding 1 g. of norit and warming gently. After filtering and cooling, the free acid is liberated by adding concentrated hydrochloric acid drop by drop till the solution is acid to congo-red paper. After allowing the liquid to stand for about half an hour, the mucic acid is filtered, washed with cold water and the melting point determined; m.p.  $206^{\circ}$  (d). Yield, 4 to 5 g.

(Dissolve a few crystals of the acid in a few drops of potassium hydroxide solution. Place a few drops of the solution, on a micros-

cope slide and observe the characteristic cubical crystals of the potassium mucate).



### Preparation 8

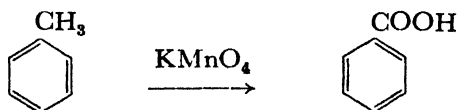
### BENZOIC ACID (FROM TOLUENE)

Potassium permanganate ... 6.2 g. (in 100 c.c. water)

Toluene ... 5 c.c.

(1 c.c. of  $\text{KMnO}_4 = 0.01$  g. of available oxygen.)

5 c.c. of sodium carbonate solution (2N) and 10 c.c. of the toluene are placed in a litre round-bottom flask fitted with a reflux condenser. The permanganate solution is added in portions of 10 c.c. from a dropping funnel while the flask is heated on an asbestos-centred wire-gauze. The contents of the flask are kept steadily boiling and the addition of permanganate is continued till no more is taken up. The flask is cooled, the precipitated manganese dioxide is filtered, the filtrate concentrated to about 25 c.c. and then saturated with sulphur dioxide till the solution is colourless. On cooling, benzoic acid crystallises out. It is filtered and recrystallised from boiling water; m.p. 121°. Yield, 3 g.



(*Note.* Oxidation of benzyl chloride to benzoic acid can be carried out similarly using the following quantities and procedure.)

Benzyl chloride ... 4 g.

Potassium carbonate ... 4 g. in 40 c.c. of water

The benzyl chloride and potassium carbonate are refluxed for an hour first and the permanganate added little by little through the condenser.

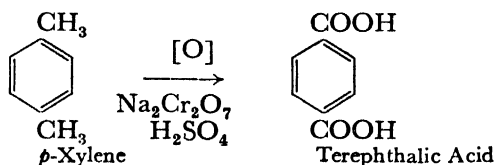
The reaction mixture is worked up as in the case of the oxidation of toluene. Yield, 4 g.

**Preparation 9****TEREPHTHALIC ACID (FROM *p*-XYLENE)**

<i>p</i> -Xylene	... 12.5 g. (15 c.c.)
Sodium dichromate	... 70 g. (in 300 c.c. of water)
Concentrated sulphuric acid	... 170 g. (92.5 c.c.)

15 c.c. of *p*-xylene, 70 g. of sodium dichromate crystals and 300 c.c. of water are placed in a 1 litre three-necked flask equipped with a reflux condenser, a mercury-sealed mechanical stirrer and a separating funnel. 170 g. (92.5 c.c.) of concentrated sulphuric acid is added dropwise through the separating funnel to the well stirred mixture at such a rate that the reaction is under control ; this usually takes 30-45 minutes. When all the acid has been introduced and the temperature begins to fall, the mixture is refluxed gently for half an hour. The reaction mixture is cooled and poured into about 500 c.c. of ice water and allowed to stand for 1 hour. The crude terephthalic acid is filtered, washed with 25 c.c. of cold water followed by 20 c.c. of ether. The acid is purified by dissolving in 5% sodium hydroxide solution (about 60 c.c. are required), the solution filtered from any chromic hydroxide and added to 225 c.c. of well-stirred 15% sulphuric acid (37 g. or 20 c.c. of concentrated sulphuric acid in 200 c.c. water). The purified acid is filtered and washed thoroughly with cold water and dried at 100°.

Terephthalic acid sublimes without melting at 300° and is almost insoluble in water and alcohol. Yield, 9 g.

**Alternative**

<i>p</i> -Xylene	... 10 c.c.
Potassium permanganate (powdered)	... 50 g.
Water	... 250 c.c.
Sodium hydroxide (2N)	... 5 c.c.

A round-bottom flask of 1 litre capacity is fitted with a Liebig's condenser ; 250 c.c. of water are measured into it followed by 5 c.c. of 2N-sodium hydroxide solution. About 20 g. of permanga-

nate are added and finally *p*-xylene. The contents are refluxed for 3-4 hours after adding two pieces of porous porcelain. Care is taken to avoid bumping by frequent swirling of the flask. When the colour of the permanganate has disappeared, further quantities of permanaganate are added till a faint pink colour persists. The flask is cooled, the mangansese dioxide is filtered off, washed with water, the filtrate and washings are concentrated, cooled and saturated with sulphur dioxide. The precipitated acid is filtered and dried. Yield 3-4 g.

[*Note:* Addition of vanadium pentoxide (0.2 g.) reduces the time of oxidation.]

### Preparation 10

#### BENZYL ALCOHOL AND BENZOIC ACID (FROM BENZALDEHYDE)

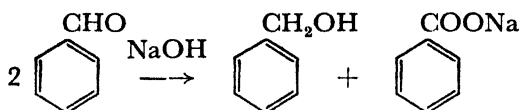
(*Cannizzaro reaction*)

Benzaldehyde (freshly distilled) ... 12.5 g.

Caustic soda ... 11.5 g. (in 8 c.c. of water).

The freshly distilled benzaldehyde and the caustic soda solution are introduced into a 100 c.c. round-bottom flask, tightly corked and shaken vigorously. An emulsion is formed which is left overnight. Water is then added to dissolve the sodium benzoate which has separated, and the flask shaken till a clear solution is obtained. The mixture is extracted with ether (30 c.c., thrice.) The ether extract which contains the benzyl alcohol is shaken with a little saturated bisulphite solution to remove any benzaldehyde and finally with sodium carbonate to remove any bisulphite. The ether extract is dried over anhydrous magnesium sulphate or anhydrous potassium carbonate and distilled on a water-bath to remove the ether. The benzyl alcohol is distilled using an air condenser, the portion coming over at 200-208° being collected separately, b.p. 205.8°. Yield, 4 to 5 g.

The alkaline solution left after extraction with ether is acidified with concentrated hydrochloric acid, cooled in ice and then the benzoic acid is filtered. The acid is recrystallised from water, m.p. 121°. Yield, about 5 g.



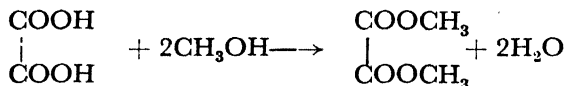


**Preparation 11****METHYL OXALATE**

Oxalic acid crystals ... 30 g.

Methyl alcohol (absolute) ... 24 g. (31 c.c.)

The finely powdered oxalic acid is spread on a clock glass (4" diam.) and weighed. It is then heated in an air oven between 110° and 120° for about an hour to drive off the water of hydration. The heating is continued (1 hour) until the loss in weight corresponds to the two molecules of water contained in the acid (roughly 8.5 g.). The anhydrous acid is mixed in a 100 c.c. round-bottom flask with the methyl alcohol and heated under reflux on a boiling water-bath for about 2 hours. The round-bottom flask is then fitted with a Young's stillhead (4 bulbs) and the contents fractionally distilled using a water-condenser at first. When the temperature reaches about 120°, the receiver is changed and the distillation continued, using an air-condenser (or removing the water from the water jacket of the condenser). The distillate coming over solidifies in the receiver (porcelain dish), is filtered and pressed by a glass stopper to remove any adhering liquid. The product is recrystallised from methyl alcohol, from which it separates in colourless plates, m.p. 54°, b.p. 163.3°. Yield, 10 g.

**Preparation 12****ETHYL ACETATE**

Alcohol (absolute) ... 28 c.c.

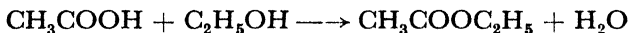
Concentrated sulphuric acid ... 13 c.c.

Glacial acetic acid ... 15 c.c.

A 200 c.c. distilling flask is fitted up as for distillation, a mixture of 13 c.c. of absolute alcohol and 13 c.c. of concentrated sulphuric acid is poured into it and 50 c.c. dropping funnel with a long stem the end of which is drawn out to a fine point is fitted through a one-holed cork to the distilling flask in such a manner that the drawn-out end just dips into the liquid. The distilling flask is heated to 140-145° in an oil or glycerine bath and a mixture of alcohol and glacial acetic acid (15 c.c. of each) is allowed to drop from the dropping funnel very slowly. When the reaction has

progressed sufficiently and a regular distillation has commenced the rate of flow of the alcohol-acid mixture is adjusted to be equal to the rate of distillation. The temperature of the bath is maintained constant at 140-145° throughout (about 4 hours) by heating it with a Bunsen burner fitted with a rose top. The distillate is now treated with a concentrated solution of sodium carbonate in a 250 c.c. round-bottom flask until there is no effervescence and the upper layer of the ester reacts acidic no longer. The layer of ester is separated by means of a separating funnel and purified as described earlier.

It is obtained as a colourless liquid with an agreeable fruity odour, b.p. 77°, sp. gr. 0.899<sup>20°</sup>. Yield, 17 g.



#### Alternative

Alcohol (absolute)	... 23 g. (30 c.c.)
Concentrated sulphuric acid	... 5 c.c.
Acetic acid, glacial	... 30 g. (29 c.c.)

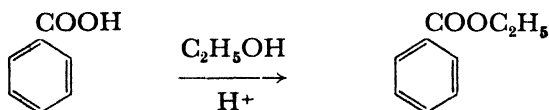
Into a 200 c.c. distilling flask, the alcohol and acetic acid are introduced first, and sulphuric acid is then added carefully with shaking and cooling under the tap. Two small pieces of porous porcelain are introduced and the side-tube is closed with a piece of rubber tubing and a glass rod. The mixture is heated under reflux on a water-bath for about ten minutes after which the flask is allowed to cool down. The condenser is now set up as for distillation, and the contents of the flask are distilled at a constant temperature of 130° by heating in an oil-bath. When no more liquid distils over the distillate is shaken with twice its volume of water in a separating funnel to remove unchanged alcohol and acid. The lower aqueous layer is drawn off and the ester is dried over anhydrous potassium carbonate (10 g.) for an hour or more. The clear liquid is transferred to another distilling flask (50 c.c.) and distilled, the fraction coming over at 76-77° being collected. Yield, 27 g.

### Preparation 13

#### ETHYL BENZOATE

Benzoic acid	... 12.5 g.
Alcohol (absolute)	... 25 g.
Concentrated sulphuric acid	... 2.5 g.

A mixture of benzoic acid, alcohol and concentrated sulphuric acid, in the proportions indicated above, is taken in a 250 c.c. round-bottom flask and boiled under reflux for about two hours. To test if esterification is complete, a few drops are poured into a little water. Oily drops of ester alone should separate without any benzoic acid crystallising simultaneously. The excess of alcohol is distilled off and the residue poured into cold water. The liquid is neutralised by adding solid sodium carbonate, a little at a time, until effervescence ceases and the oil is then extracted with ether. The ether extract is dried over anhydrous potassium carbonate or calcium chloride and the ether removed by distillation from a hot water-bath. The residual oil is distilled using an air-condenser, collecting the liquid passing over between 210-214°. It is a colourless liquid with a characteristic pleasant smell ; b.p. 213° ; sp. gr. 1.047<sup>20°</sup>. Yield, 12 g.



### Preparation 14

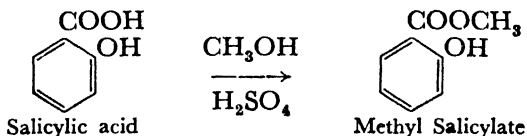
#### METHYL SALICYLATE

Salicylic acid	... 8.5 g.
Methyl alcohol	... 15 c.c.
Concentrated sulphuric acid	... 2.5 c.c.

The salicylic acid and methyl alcohol are taken in a 100 c.c. round-bottom flask and the sulphuric acid added gradually with shaking. The flask is fitted with a reflux condenser and the contents heated on a boiling water-bath for 3 hours. Excess of methyl alcohol is then distilled off on the water-bath, 20 c.c. water added to the reaction mixture in the flask and the whole then transferred to a separating funnel. Enough ether is then added to dissolve the ester formed and the ether layer separated from the aqueous layer. The aqueous layer is then extracted with some more ether. The combined ether extract is then washed repeatedly with dilute sodium carbonate solution till free from acid and finally with water. The ether solution is then dried over anhydrous sodium sulphate. It is then filtered into a dry distilling flask, the

ether is removed over a water-bath and the ester left behind is purified by distillation in a flask of suitable size.

Methyl salicylate is a colourless liquid with fragrant smell, b.p.  $223-224^{\circ}/760$  mm. Yield, 8 g.



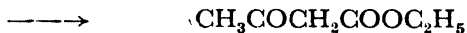
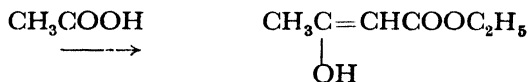
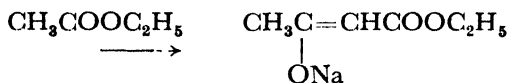
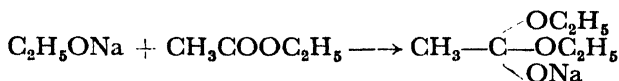
### Preparation 15

#### ETHYL ACETOACETATE

Ethyl acetate	... 75 g.
Sodium (metal)	... 7.5 g.
Glacial acetic acid	... 25 g.

*Note:* To obtain a good yield the experiment should be started in the morning and completed by evening. The apparatus should be quite dry and assembled even on the previous day and protected from moisture by a calcium chloride tube.

The cleaned sodium in the form of thin slices or pressed wire is quickly introduced into a dry 500 c.c. round-bottom flask fitted with a condenser and carrying a calcium chloride guard tube. The flask is surrounded by cold water and the ethyl acetate, purified as described earlier and kept overnight over anhydrous calcium chloride, is filtered, and added all at once through the condenser, replacing the guard tube after the addition is over. There is a brisk action initially after which the flask is heated on a water-bath till all the sodium has disappeared (four hours). The liquid while still warm is treated gradually with glacial acetic acid diluted with its own volume of water till it is just acid to litmus. The neutralised liquid is transferred to a separating funnel (500 c.c.) an equal volume of saturated brine is added and the mixture thoroughly shaken. The upper layer consisting of a mixture of ethyl acetate and ethyl acetoacetate is separated, dried and distilled on a boiling water-bath to remove ethyl acetate. The residue is distilled under diminished pressure using a good water-pump, It is a colourless liquid possessing fruity smell ; b.p.  $86-90^{\circ}/30$  mm. ; sp. gr.  $1.025^{20}$ . Yield, 9-10 g. The residue in the flask is dehydracetic acid.

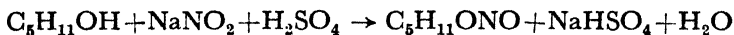


### Preparation 16

#### AMYL NITRITE

Amyl alcohol (b.p. 130°)	... 15 g. (18.5 c.c.)
Sodium nitrite (powdered)	... 15 g.
Concentrated sulphuric acid	... 9 g. (5 c.c.)

The amyl alcohol is measured into a 250 c.c. round-bottom flask after which the sodium nitrite is added and the two are thoroughly mixed. The mixture is cooled in ice and concentrated sulphuric acid added drop by drop from a dropping funnel with continuous shaking (one hour). In the later stages the addition of sulphuric acid is made slowly owing to the tendency of the reaction to become vigorous. After the addition of the acid is over, the contents of the flask are taken in a separating funnel, the upper layer of amyl nitrite is separated, and the lower layer diluted with a little water in the separating funnel itself whereby some more amyl nitrite is obtained, which is separated and added to the main bulk. The amyl nitrite is dried over anhydrous calcium chloride in the separating funnel, filtered into a clean distilling flask (50 c.c.) and distilled. The portion coming over between 95-100° is collected, weighed and sealed in a tube. It is a yellowish green liquid with a penetrating and sweet smell; b.p. 99°; sp. gr. 0.872<sup>20°</sup>. Yield, 13 g.

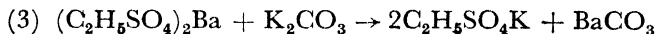
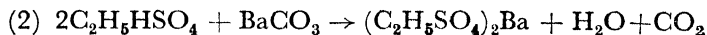
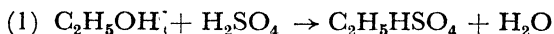


### Preparation 17

#### POTASSIUM ETHYL SULPHATE

Alcohol (absolute)	... 20 c.c. (16 g.)
Concentrated sulphuric acid	... 10 c.c.

The alcohol is measured into a 100 c.c. round-bottom flask and the sulphuric acid added slowly with constant stirring. The flask is fitted with a reflux condenser and heated on a boiling water-bath for an hour. The liquid is cooled and poured slowly with stirring into 200 c.c. of water contained in a 400 c.c. beaker. This solution containing ethyl sulphuric acid, alcohol and free sulphuric acid is treated with barium carbonate in small quantities at a time till no more carbon dioxide is evolved. The free sulphuric acid is removed as the insoluble barium sulphate while the ethyl sulphuric acid is converted into the soluble barium ethyl sulphate. The barium sulphate is allowed to settle and the supernatant liquid filtered through a fluted filter. The precipitated barium sulphate in the beaker is washed twice with hot water (20 c.c.) and the wash liquid filtered. The combined filtrates are heated to boiling in a litre beaker and a strong solution of potassium carbonate added until the solution shows a slight alkalinity. The liquid is filtered hot in a Buchner funnel and the precipitate washed twice with small amounts of hot water. The filtrate is evaporated on a water-bath to the crystallising point and cooled. The crystals are filtered and washed with a little cold alcohol. The salt is purified by crystallisation from alcohol using about 100 c.c. and employing a small Soxhlet extractor. It is obtained in colourless crystals, easily soluble in water. Yield, 12 g.



### Preparation 18

#### ACETYL CHLORIDE

Glacial acetic acid ... 24 g. (23 c.c.)

Phosphorus trichloride ... 21 g. (13 c.c.)

It is necessary to have all the apparatus used in this preparation perfectly dry. One or two spare distilling flasks (100 c.c.) should be kept ready in a dry condition and used when required.

The experiment should be performed in a fume cupboard with a good draught.

A dry distilling flask (100 c.c.) fitted with a one-holed cork carrying a 50 c.c. dropping funnel is connected to a Liebig's condenser, the lower end of which is attached by means of a tight-fitting cork to another distilling flask (100 c.c.) which serves as the receiver. A calcium chloride tube is attached to the side-tube of the receiver to keep off external moisture (Fig. 40). 23 c.c. of

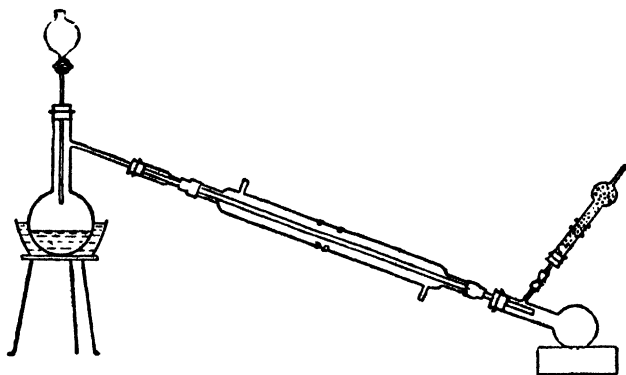
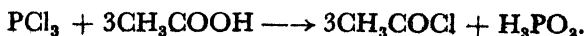


Fig. 40

glacial acetic acid are measured into the distilling flask and 13 c.c. of the trichloride into the dropping funnel. The reaction flask is surrounded by a cold water-bath to begin with and the trichloride is added drop by drop. After an interval of about an hour, the water-bath is heated to 40-50° and kept at this temperature till no further evolution of hydrogen chloride is noticed. The water-bath is then heated to boiling to distil off the acetyl chloride. When the distillation is completed the receiver is fitted with a cork carrying a thermometer and the acetyl chloride redistilled after adding a few pieces of porous porcelain. The liquid distilling between 53-56° is collected in another distilling flask as before. It is a colourless liquid with a pungent smell, fuming in air ; b.p. 52° ; sp. gr. 1.105<sup>20°C</sup>. Yield, 20 g.



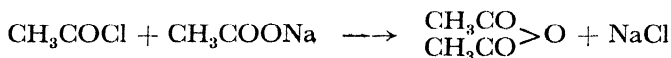
**Preparation 19**

## ACETIC ANHYDRIDE

Sodium acetate (freshly fused)	... 28 g.
Acetyl chloride	... 20 c.c.

The apparatus for this experiment is assembled exactly as in the previous experiment, observing the same precautions.

About 40 g. of the commercial fused sodium acetate are heated in a porcelain basin (12 cm. diam.) until completely melted; the liquid is poured into a dry mortar, allowed to cool, powdered and kept in a desiccator. 28 g. of this sodium acetate are introduced into the distilling flask and the acetyl chloride (20 c.c.) gradually added from a dropping funnel. During the addition the flask is cooled in water. The contents are stirred thoroughly with a glass rod, the distilling flask is closed with a cork and heated gently over a small flame which is kept moving to prevent the flask from cracking. When the distillation has stopped, 2 g. of fused sodium acetate are added to the receiver and the liquid redistilled using a thermometer and collecting the portion between 135-140°. It is a colourless liquid with an irritating smell, b.p. 139.6°; sp. gr. 1.082<sup>20</sup>. Yield, 21 g.

**Preparation 20**

## ACETAMIDE

Ammonium acetate	... 25 g.
Glacial acetic acid	... 21 g. (20 c.c.)

The crystals of ammonium acetate which are hygroscopic are pressed between folds of filter paper and dried by keeping in a desiccator. The dry ammonium acetate and glacial acetic acid are introduced into a 100 c.c. round-bottom flask fitted with a reflux condenser and refluxed on wire-gauze for an hour. The reflux condenser is removed and the flask fitted with a small fractionating column (two-bulbs) carrying a thermometer and attached to a condenser and receiver. The liquid is distilled very slowly and at such a rate that the temperature does not rise above



104-105° during the time that 6-7 c.c. of distillate collect. The distillation is continued very slowly as before till the volume of the distillate is about 25 c.c., the time taken for this part of the experiment being about 2½ hours. The residue in the flask is acetamide ; it is transferred after cooling to a distilling flask (50 c.c.) and distilled using an air-condenser, collecting the distillate in three fractions, (a) up to 195° (b) from 195° to 215° and (c) between 215° and 225°. On cooling, the fractions (b) and (c) solidify. The crystals are filtered with suction and dried by pressing on filter paper and weighed.

A small amount (2 to 3 g.) is crystallised from benzene or ether or a mixture of benzene and ethyl acetate (3 c.c. of benzene and 1 c.c. of ethyl acetate) by warming on a water-bath and cooling rapidly in ice. The crystals are filtered and pressed between folds of filter paper. They have a peculiar smell and are very hygroscopic ; m.p. 82°, b.p. 222°. Yield, 14 g.

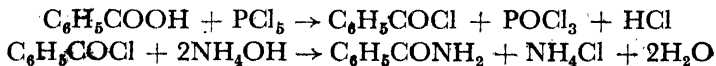


## Preparation 21

### BENZAMIDE

Benzoic acid	... 7 g.
Phosphorus pentachloride	... 13 g.

The benzoic acid is added to the phosphorus pentachloride contained in a dry 100 c.c. distilling flask and mixed thoroughly with a glass rod. Dense clouds of hydrogen chloride are given off and when the reaction slackens, the phosphorus oxychloride is distilled off at 107-110°. The residual liquid which is benzoyl chloride is transferred to a dropping funnel and added drop by drop to 25 c.c. of liquor ammonia contained in a beaker and cooled in ice water. Much heat is evolved during the addition. When the addition is over the liquid is cooled and the precipitated benzamide is filtered and recrystallised from hot water. It crystallises in colourless plates, m.p. 130°. Yield, 5 g.



**Preparation 22**

## GLYCINE (AMINOACETIC ACID)

Chloracetic acid	... 20 g. (in 20 c.c. water)
Ammonium carbonate (commercial)	72 g. (in 75 c.c. water)
Ammonia (sp. gr. 0.88)	... 40 c.c.

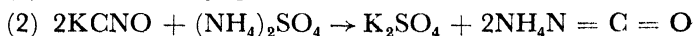
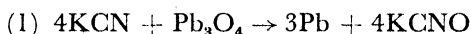
72 g. of commercial ammonium carbonate are dissolved in 75 c.c. of warm water (40-50°) in a 500 c.c. round-bottom flask. The contents are cooled to room temperature and 40 c.c. of liquor ammonia are added. Then a solution of 20 g. of chloracetic acid in 20 c.c. of water is introduced dropwise into the flask with constant swirling of the contents of the flask. The flask is closed with a solid rubber stopper. The stopper is held in place by fixing a thin copper wire. Care is taken not to moisten the portion of the stopper in contact with glass as this lubrication will cause the stopper to slide out of the flask. The flask is allowed to stand 48 hours at room temperature. The mixture is then transferred to a distilling flask and concentrated *in vacuo* (water-pump) to about  $\frac{1}{4}$  the original volume. If the solution is not colourless, it is warmed with about 1 g. of decolourising carbon and filtered. The cold filtrate is treated with 150 c.c. of methyl alcohol and allowed to cool in a refrigerator for 4-6 hours. Crude glycine crystallises out, along with some ammonium chloride. Most of the latter is removed by suspending the crystals in 60 ml. of methyl alcohol, stirring well, filtering and washing with a little methyl alcohol and finally with ether. The yield is about 10 g. Further purification may be carried out as follows: The glycine (10 g.) is dissolved in 20 c.c. of warm water, stirred with 2 g. norit and filtered. The glycine is precipitated by the addition of 80 c.c. of methyl alcohol, filtered and washed with methyl alcohol and then ether and dried in air. Glycine darkens at 237° and melts at 240° with decomposition. Yield, 12 g.

**Preparation 23**

## UREA

Potassium cyanide	... 25 g.
Red lead	... 70 g.
Ammonium sulphate	... 12.5 g.

The potassium cyanide is fused in a clean sand tray and the red lead added gradually in quantities of 5 g. and stirred with a stout iron wire. There is a tendency for the mass to froth up. When the mass melts quietly, it is poured on to another sand tray and allowed to cool. The solid is powdered and the cake of metallic lead is separated. The crude cyanate is extracted with 100 c.c. of cold water and filtered through a fluted filter after an hour. A saturated solution of the ammonium sulphate is quickly added to the filtrate and the liquid evaporated to dryness on a water-bath in a 12 cm. basin with occasional stirring. The dry solid is extracted with 100 c.c. of alcohol in a Soxhlet extractor. Most of the alcohol is removed by distillation on a water-bath, after which the residue is transferred to a beaker for crystallisation. Colourless prisms are obtained, m.p.  $133^{\circ}$ . Yield, 5 to 6 g.



### Alternative

Potassium ferrocyanide	... 50 g.
Potassium dichromate	... 37 g.
Ammonium sulphate	... 25 g. (in 40 c.c. water)

The potassium ferrocyanide is finely powdered and dried in the steam or air oven at  $100\text{--}110^{\circ}$  for about 2 to 3 hours. A sample is heated in a test-tube to see if all water has been expelled. The dichromate is dried, powdered well and mixed with the ferrocyanide. A clean sand tray is heated strongly over a Teclu burner or blast lamp and the mixture is poured in five gram lots on to the sand tray. The mass glows brightly and when the glow has disappeared, a fresh portion is added so that it falls on a fresh surface. The residue is powdered when warm, and extracted with a mixture of 200 c.c. of alcohol, 45 c.c. of water and 25 c.c. of methanol in a Soxhlet. The filtered liquid is at once mixed with a solution of ammonium sulphate in hot water and the separating potassium sulphate is filtered off. The alcohols are distilled off and can be used to extract the urea. The residue containing the inorganic salts and urea is evaporated to dryness on a water-

bath, and the dry residue is extracted in a Soxhlet with the recovered alcohol which has been dried over quicklime and distilled. The urea is recovered as before. Yield, 8 g.

### Preparation 24

#### ACETANILIDE

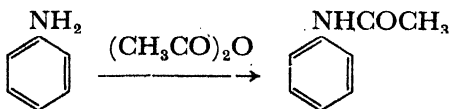
Aniline (freshly distilled)	... 5 g. (5 c.c.)
Glacial acetic acid	... 6.5 g. (6 c.c.)
Sodium acetate (freshly fused)	... 2 g.

The aniline and acetic acid are introduced into a 50 c.c. round-bottom flask fitted with a long air condenser. 2 g. of freshly fused sodium acetate are then added and the mixture gently refluxed by heating on a wire gauze. Part of the water formed and a little acetic acid escape at the top. The heating is continued for 2-3 hours. The mixture is poured while hot into 100 c.c. water contained in a beaker with vigorous stirring. After cooling, the precipitate is filtered, and washed with cold water. The slightly coloured substance is dissolved in about 150 c.c. of boiling water; heated with 1 g. animal charcoal and filtered through a hot water funnel. The filtrate is allowed to cool. The acetanilide crystallises out in rhombic plates, m.p. 114°. Yield, 6 g.

#### Alternative

Aniline (freshly distilled)	... 5 c.c.
Acetic anhydride	... 8 c.c.

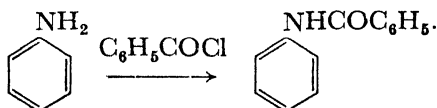
The freshly distilled aniline and acetic anhydride are taken in a 50 c.c. round-bottom flask fitted with a reflux condenser. The mixture is refluxed for 15 to 20 minutes, and then the hot liquid is poured in a thin stream with stirring on crushed ice in a beaker. The white solid that separates is filtered, washed with water and then recrystallised as previously. Yield, 7 g.



**Preparation 25****BENZANILIDE**

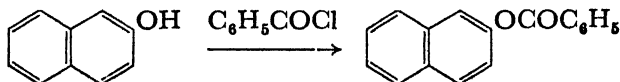
Aniline	... 2.5 c.c.
Sodium hydroxide (10%)	... 22 c.c.
Benzoyl chloride	... 3.5 c.c.

2.5 c.c. of aniline and 22 c.c. of 10% aqueous sodium hydroxide solution are placed in a 100 c.c. conical flask fitted with a good cork and 3.5 c.c. of benzoyl chloride are then added, the flask stoppered, and shaken vigorously for 10-15 minutes. Heat is evolved in the reaction. The crude benzoyl derivative separates as a white powder. When the reaction is complete (*i.e.*, when the odour of benzoyl chloride can no longer be detected) the reaction mixture is made alkaline if necessary, and the product filtered and washed with water. Recrystallisation from alcohol affords crystals, m.p. 162°. Yield, 4.5 g.

**Preparation 26** **$\beta$ -NAPHTHYLBENZOATE**

$\beta$ -Naphthol	... 2 g.
Sodium hydroxide (10%)	... 20 c.c.
Benzoyl chloride	... 3 c.c.

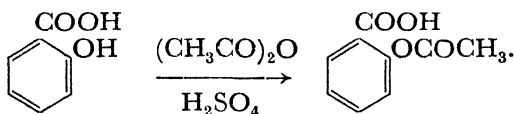
Proceed exactly as in the previous experiment.  $\beta$ -Naphthyl benzoate crystallizes from dilute alcohol ; m.p. 107°. Yield, 4 g.



**Preparation 27****ASPIRIN (ACETYLSALICYLIC ACID)**

Salicylic acid	... 5 g.
Acetic anhydride	... 7 c.c.

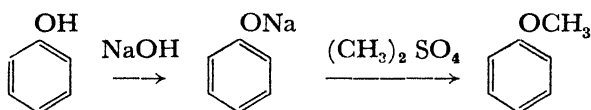
5 g. of salicylic acid and 7 c.c. of acetic anhydride are mixed in a 100 c.c. conical flask and 3 drops of concentrated sulphuric acid are added. The mixture is warmed on a water bath at 50-60° with occasional shaking. 50 c.c. of water are then added the mixture stirred well and filtered. The crude aspirin is purified by dissolving in about 15 c.c. of hot alcohol and pouring into about 40 c.c. of warm water. The solution which then becomes turbid is warmed to give a clear solution and then allowed to cool slowly. The needles which separate are filtered. Yield, 7 g. Acetylsalicylic acid decomposes when heated and does not possess a true, clearly defined melting point. Decomposition points ranging from 128° to 135° have been recorded.

**Preparation 28****ANISOLE**

Phenol	... 10 g.
Dimethyl sulphate (washed free from acid)	... 17 c.c.
Caustic soda (10% solution)	... 50 c.c.

The phenol is dissolved in the sodium hydroxide solution contained in a 250 c.c. round-bottom flask and the dimethyl sulphate is added from a dropping funnel dropwise with continuous mechanical stirring. As the methylation proceeds, the temperature rises and care is therefore taken to see that the reaction mixture is maintained below 50°. When all the dimethyl sulphate has

been added, the reaction mixture is treated with more caustic soda solution to make it just alkaline. The stirring is continued for a further half hour. The flask is then fitted with a water condenser and heated on a boiling water bath for about an hour. Any excess of dimethyl sulphate will be decomposed by this treatment. If the solution is not alkaline at this stage more of caustic soda solution is added until it is alkaline. The contents of the flask are cooled and transferred into a 250 c.c. separating funnel and extracted thrice with ether (30 c.c. each time). The combined ether extract is dried over anhydrous sodium sulphate. The ether solution is then filtered into a distilling flask. The ether is removed over a water bath and the anisole then transferred to a small distilling flask (25 c.c.) and distilled. It is a colourless oil with a pleasant aromatic odour ; b.p.  $156^{\circ}$ . Yield, 10 g.



*Note:* Dimethyl sulphate is a deadly poison and contact with skin and inhalation of its vapours should be avoided. Care has to be taken not to inhale it. Reactions with dimethyl sulphate should be carried out in a fume cupboard.

Commercial dimethyl sulphate may contain free acid which should be removed by repeated washing with ice water.

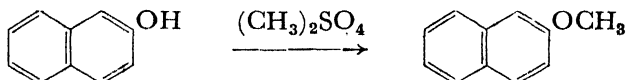
### Preparation 29

#### $\beta$ -NAPHTHYL METHYL ETHER

$\beta$ -Naphthol	... 5 g.
Caustic soda	... 4 g. (dissolved in 40 c.c. water)
Dimethyl sulphate	... 4 c.c.

$\beta$ -Naphthol is dissolved in the caustic soda solution contained in a 100 c.c. round-bottom flask. The solution is cooled to room temperature and the dimethyl sulphate is added a little at a time while the flask is cooled under the tap so that the temperature does

not rise. The mixture is finally warmed on the water-bath for half an hour to decompose the excess of methyl sulphate, the solution being always kept alkaline. The ether which separates on cooling as a solid is filtered off, washed with water and recrystallised from alcohol. It crystallises in lustrous plates with a pleasant odour, m.p.  $72^{\circ}$ . Yield, 5.5 g.

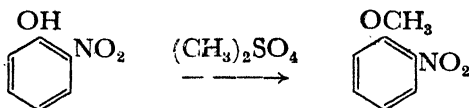


### Preparation 30

#### O-NITROANISOLE

O-Nitrophenol	... 17.5 g.
Dimethyl Sulphate	... 24.2 g.
Sodium Carbonate (anhydrous)	... 14.0 g.
Toluene	... 75 c.c.

In a one-litre bolt-head flask fitted with stirrer (mercury seal), condenser and dropping funnel, 17.5 g. of o-nitrophenol dissolved in 75 c.c. of dry toluene are taken. 14 g. of finely powdered sodium carbonate (90 mesh, anhydrous) are then added and the mixture heated to  $100^{\circ}$  with stirring. 24 g. of pure dry dimethyl sulphate are added dropwise and after addition is over, the mixture heated at  $110\text{--}120^{\circ}$  for 6 hours. The mixture is then cooled, and treated with 100 c.c. water. The toluene layer is separated and washed with dilute sodium hydroxide solution for removal of unreacted material. The toluene is then distilled off using an oil bath and the residual liquid distilled under reduced pressure; b.p.  $150\text{--}151^{\circ}/2\text{ m.m.}$  Yield, 17 g.



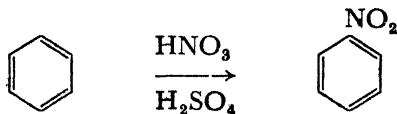


**Preparation 31****NITROBENZENE**

Benzene	... 13 c.c.
Concentrated nitric acid	... 18 c.c.
Concentrated sulphuric acid	... 18 c.c.

The concentrated nitric acid is measured into a 250 c.c. conical flask and the sulphuric acid is added a little at a time while cooling the flask under the tap. When the mixture is quite cold it is added from a separating funnel drop by drop to 13 c.c. of benzene contained in a 250 c.c. round-bottom flask. During the addition, the flask should be occasionally shaken and cooled under the tap so that the temperature does not rise above 50°. When the addition is over, the flask is fitted with an air condenser and heated by immersion in a water-bath maintained at 50-60° for about half an hour. The flask is shaken from time to time. To see whether nitration is complete a drop of the mixture is added to 5 c.c. of water contained in a test-tube and if the drop sinks to the bottom the reaction is considered over. After cooling, the contents of the flask are poured into about 300 c.c. of cold water in a beaker, the mixture is stirred well in order to wash out as much acid as possible from the nitrobenzene, and allowed to stand. When the nitrobenzene has settled to the bottom, the acid liquor is poured off as completely as possible and the residual liquid is transferred to a separating funnel. The lower layer of nitrobenzene is run off and freed from acid by washing with sodium hydroxide solution.

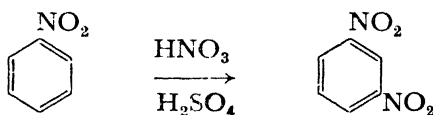
The nitrobenzene is dried by addition of calcium chloride (2-3 g.) and purified by distillation. The first runnings consisting chiefly of a little benzene and traces of water are neglected and the portion distilling over 208--210° is collected. Pure nitrobenzene is a clear, pale yellow liquid, b.p. 210°. Yield, 16 g.



**Preparation 32*****m*-DINITROBENZENE**

Nitrobenzene	... 12 g.
Concentrated sulphuric acid	... 30 g.
Fuming nitric acid (sp. gr. 1.5)	... 21 g.

The nitric acid is first measured into a 500 c.c. round-bottom flask and the sulphuric acid added a little at a time, cooling the flask during the addition. The nitrobenzene is added 4 c.c. at a time and thoroughly shaken after each addition. The mixture is heated on a boiling water-bath for about an hour. A few drops are poured into a test-tube containing a little water and if the reaction is complete, the dinitrobenzene separates as a hard solid. Otherwise the heating is continued for some more time. The contents of the flask while still warm are then poured in a thin stream into about 300 c.c. of cold water contained in a beaker with vigorous stirring. The solid dinitrobenzene is filtered and washed well with water. It is then stirred with 40-50 c.c. of 10% sodium hydroxide on a water bath at 80° for an hour; cooled and filtered and recrystallised from rectified spirits. It crystallises in long colourless needles; m.p. 90°. Yield, 12 g.

**Alternative**

Nitrobenzene	... 10 g. (8.2 c.c.)
Sodium nitrate (commercial)	... 14 g.
Concentrated sulphuric acid	... 46 g. (25 c.c.)

The nitrobenzene and the sodium nitrate are taken in a 300 c.c. round-bottom flask and the sulphuric acid gradually added, while the mixture is shaken from time to time. The flask is fitted with an air-condenser and heated on a water-bath. At about 80° the reaction commences when, the flask with the

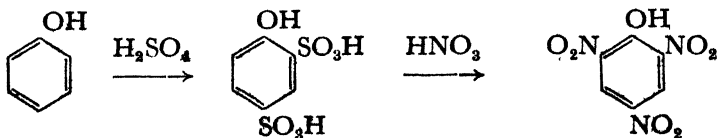
condenser is removed and the contents well shaken. The reaction becomes vigorous and then subsides slowly. The mixture is heated on a wire gauze for a few minutes to ensure complete liberation of nitric acid. Final heating is done on a water-bath after removing the condenser, till a drop or two poured into 2 c.c. of water solidifies. While still hot the contents are poured with vigorous stirring into about 400 c.c. of water. The flask is washed with a little water and the washings also added to the main bulk. The solid is filtered, washed with water and dried. Yield, 11.5 g. The compound is purified as described previously.

### Preparation 33

#### PICRIC ACID

Phenol	... 10 g.
Concentrated sulphuric acid	... 20 g. (11.5 c.c.)
Concentrated nitric acid	... 50 g. (sp. gr. 1.5, 34 c.c.)

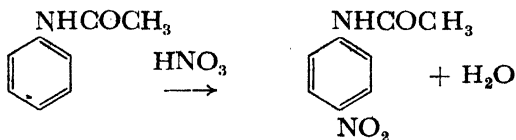
The phenol is added to concentrated sulphuric acid contained in a 100 c.c. round-bottom flask and dissolved by warming on a water-bath or over a free flame so that the temperature does not rise above  $110^{\circ}$ . The contents of the flask are kept at this temperature for about fifteen minutes and then cooled. Meanwhile the nitric acid is measured into a 250 c.c. round-bottom flask and cooled in ice-water. The phenol-sulphonic acid is transferred to a dropping funnel, from which it is added in drops to the nitric acid with constant shaking. A considerable amount of heat is generated during the addition and it is necessary that the temperature does not rise above  $50-60^{\circ}$ . When the reaction has moderated the contents are heated on a boiling water-bath for two hours. On cooling, picric acid separates as a yellow crystalline mass. The liquid is diluted with water (500 c.c.) and filtered. The product is washed well with cold water and recrystallised from boiling water containing a little hydrochloric acid. It crystallises on cooling in yellow needles, m.p.  $121-122^{\circ}$ . Yield, 15 g.



**Preparation 34*****p*-NITRANILINE****(a) *p*-Nitroacetanilide.**

Acetanilide	... 15 g.
Glacial acetic acid	... 15 c.c.
Concentrated sulphuric acid	... 30 c.c.
Fuming nitric acid	... 6 c.c. ( $d = 1.5$ )

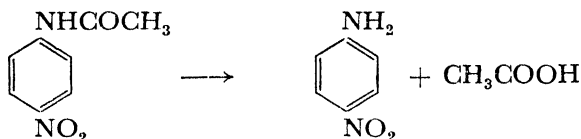
The acetanilide is dissolved in the glacial acetic acid in a wide-mouthed bolt-head flask of capacity 250 c.c. The sulphuric acid is then added and the mixture is well cooled in a freezing mixture of ice and salt. The fuming nitric acid also cooled is added from a dropping funnel slowly so that the temperature does not rise above 20°. After the addition of the acid the mixture is stirred mechanically for an hour and poured on to a mixture of 50 c.c. of water and 50 g. of ice. The product is then allowed to stand for half an hour, filtered and washed with water. This is freed from any *o*-nitrocompound by stirring into 100 c.c. of water, adding sufficient sodium carbonate till the liquid becomes alkaline to litmus and then boiling. The para-compound is unaffected, while the ortho is hydrolysed and is filtered off while still warm and washed with water. A small quantity (1 g.) is recrystallised from alcohol while the rest can be used for the succeeding preparation ; m.p. 214°. Yield, 17 g.

**(b) *p*-Nitriline.**

<i>p</i> -Nitroacetanilide	... 15 g.
Concentrated hydrochloric acid	... 38 g.

The *p*-nitroacetanilide is boiled with the hydrochloric acid in a 250 c.c. round-bottom flask fitted with an air-condenser till the liquid remains clear on dilution with water. The *p*-nitriline

is present as the hydrochloride and the free base is liberated by adding excess of ammonia. When cold the yellow precipitate is filtered and washed with a little cold water. It is practically pure but may be recrystallised from water, and comes out in yellow needles; m.p. 148°. Yield, 12-13 g.



### Preparation 35

#### 2 : 4-DINITROPHENOL

##### (1) 2 : 4-Dinitrochlorobenzene

Chlorobenzene	... 14 g. (12.5 c.c.)
Con. Sulphuric acid	... 56 g. (30.5 c.c.)
Nitric acid	... 20 c.c. (12 c.c. fuming 8 c.c. con. acid sp. gr. 1.42.)

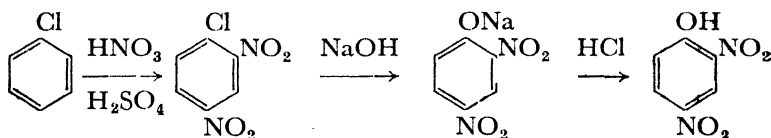
The chlorobenzene is measured into a 250 c.c. round-bottom bolt-head flask and half the quantity of sulphuric acid is added. The mixture is warmed on a water bath and stirred mechanically. The rest of the sulphuric acid is added little by little to the nitric acid with cooling under tap. The acid mixture is transferred to a 50 c.c. dropping funnel and added drop by drop so that the temperature remains below 100°. After the addition is over, the reaction mixture is stirred for an hour on a water-bath maintained at a gentle boil. The reaction is completed by heating for another hour at 120° in an oil bath, using an air condenser. The liquid is partly cooled and poured on to crushed ice contained in a 600 c.c. beaker and stirred. The solid product is filtered, washed well with cold water and pressed. It is purified by crystallisation from alcohol. Yield 16-17 g; m.p. 52-53°.

(It is advisable to use gloves in this preparation. Contact of the substance with the skin may cause dermatitis.)

(2) **2 : 4-Dinitrophenol**

2 : 4-dinitrochlorobenzene ... 10 g.  
Sodium carbonate (anhydrous) ... 12.5 g. (in 100 c.c. water)  
Sodium hydroxide ... 5.2 g. (in 100 c.c. water)

The sodium carbonate or hydroxide is dissolved in 100 c.c. of water contained in 250 c.c. round bottom flask, the 2 : 4-dinitrochlorobenzene is added and the mixture heated using a water-cooled condenser till the oily layer disappears, and the liquid becomes clear (about 4 hours). The clear liquid is filtered hot using a Büchner funnel and the filtrate acidified with hydrochloric acid. On cooling, the dinitrophenol separates. It is filtered and crystallised from hot water ; m.p. 112-113°. Yield, 8 g.

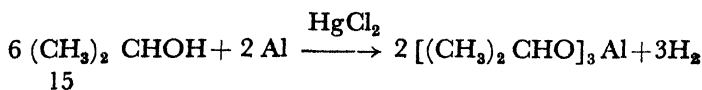


**Preparation 36**

ALUMINIUM ISOPROPOXIDE

Aluminium (wire or turnings) ... 20g.  
Isopropyl alcohol ... 240 c.c.  
Mercuric chloride ... 1g.

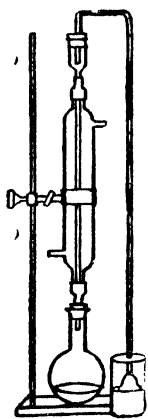
A mixture of 20g. of aluminium wire or turnings, 240 c.c. of anhydrous isopropyl alcohol and 1 g. of mercuric chloride, is heated to gentle reflux on a water-bath for 10-20 minutes until a vigorous exothermic reaction sets in. It is necessary to cool the reaction flask suitably at this stage. Reflux is then maintained for 6-7 hours. The reaction mixture is distilled *in vacuo* using an oil bath, the aluminium isopropoxide passing over as a colourless viscid liquid at 140-150/1.2 m.m. The distillate solidifies slowly to a colourless solid m.p. 118. Yield, 130 g.



**Preparation 37****BROMOBENZENE**

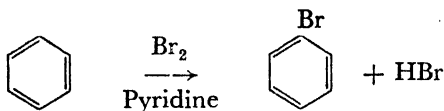
Benzene	... 12.5 g.
Bromine	... 30 g. (10 c.c.)
Pyridine	... 0.5 c.c.

The substances are introduced into a 250 c.c. round-bottom flask fitted with an upright reflux condenser to the mouth of which a one-holed cork is fixed carrying a long tube bent twice at right angles to lead away the hydrogen bromide formed (Fig. 41). The hydrogen bromide along with a little bromine is best absorbed in water. When the reaction has slowed down, the flask is heated on a water-bath at 60-70° till bromine has completely disappeared and the evolution of hydrogen bromide has nearly ceased. The contents of the flask are cooled and poured into excess of dilute caustic soda solution (10%) contained in a separating funnel, and shaken. The lower layer of bromobenzene is drawn off, dried over calcium chloride in the separating funnel till perfectly clear and the clear liquid decanted and distilled over a free flame. Unreacted benzene passes over first, the temperature then rising rapidly. The portion boiling at 150-160° is collected. It is a colourless liquid, b.p. 156°; sp. gr. 1.497<sup>20°</sup>. Yield, 15 g.

**Fig. 41**

**Bromobenzene** 150-160° is collected. It is a colourless liquid, b.p. 156°; sp. gr. 1.497<sup>20°</sup>. Yield, 15 g.

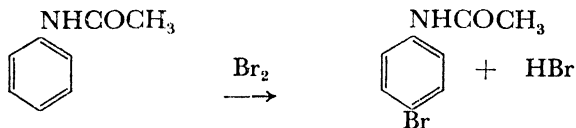
Pyridine acts here as the halogen carrier and should be added last through the condenser.



**Preparation 38*****p*-BROMOANILINE****(1) *p*-Bromoacetanilide**

Acetanilide	... 5 g.
Glacial acetic acid	... 20 c.c.
Bromine	... 6.7 g. (2.1 c.c. in 30 c.c. of glacial acetic acid.)

The finely powdered acetanilide is dissolved in 20 c.c. of cold glacial acetic acid contained in a 125 c.c. conical flask. The liquid bromine is measured from a burette into 30 c.c. of glacial acetic acid contained in a separating funnel, which is shaken gently and cautiously to get a solution of uniform concentration. The bromine solution is added slowly to the acetanilide with constant shaking to ensure thorough mixing. After the addition is over, the contents of the flask are kept aside for about 15 minutes. The pale reddish-brown solution is poured into about 200 c.c. of water contained in a beaker, and a few pieces of ice are added. The mixture is stirred and the precipitated *p*-bromoacetanilide is filtered washed with cold water and dried. About 1 g. is recrystallised from alcohol, while the rest is used for the preparation of *p*-bromoaniline. Colourless crystals, m.p. 167°. Yield, 8 g.

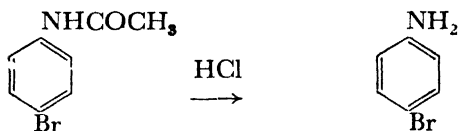
**(2) *p*-Bromoaniline**

<i>p</i> -Bromoacetanilide	... 5 g.
Concentrated hydrochloric acid	... 15 c.c.

The *p*-bromoacetanilide is boiled with the hydrochloric acid in a 100 c.c. round bottom flask fitted with a reflux condenser, till a test portion of the liquid remains clear on dilution with water. The *p*-bromoaniline is present as the hydrochloride. After hydrolysis 20 c.c. of water are added to the contents of the flask and the free base is liberated by adding strong ammonia till the



mixture gives a distinct smell of ammonia or by adding solid sodium carbonate till there is no effervescence. A colourless oily substance separates which goes to a solid after adding a few pieces of ice and stirring. The solid is filtered, washed with water and crystallised from dilute alcohol ; m.p. 66°. Yield, 3 to 4 g.

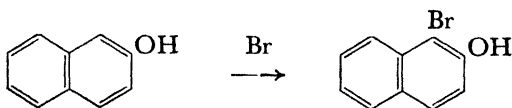


### Preparation 39

#### 1-BROMO-2-NAPHTHOL

$\beta$ -Naphthol	... 7.2 g.
Bromine	... 8 g.

A solution of 8 g. bromine in 10 c.c. glacial acetic acid is added dropwise to a solution of 7.2 g. of  $\beta$ -naphthol in 35 c.c. of acetic acid, cooling the reaction mixture in a cold water bath. The solution is then poured into 200 c.c. of water and the precipitated solid product is washed with water and recrystallised from alcohol ; m.p. 80-81°. Yield, 10 g.



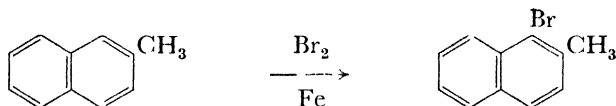
### Preparation 40

#### 1-BROMO-2-BROMOMETHYL NAPHTHALENE

##### (a) 1-BROMO-2-METHYL NAPHTHALENE

2-Methyl naphthalene	... 14g.
Bromine	... 16g.

To a solution of 14 g. of 2-methylnaphthalene in 30 c.c. carbon tetrachloride a crystal of iodine and a pinch of iron powder are added. The mixture is cooled to  $0^{\circ}$  and treated dropwise with a solution of 16 g. bromine in 30 c.c. carbon tetrachloride. The reaction mixture is stirred mechanically during the addition and the flask is covered with black paper to exclude light. The temperature is not allowed to rise above  $5^{\circ}$ . The mixture is left overnight and is then washed successively with 10% sodium hydroxide solution and water. After drying over calcium chloride, the solvent is removed and the residual liquid distilled. 1-Bromo-2-methylnaphthalene passes over at 152-156/14 mm. Yield, 18g.

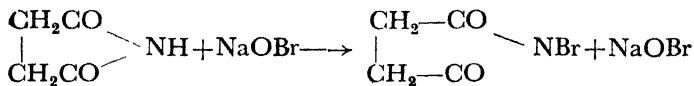


(b) N-BROMOSUCCINIMIDE

Succinimide ... 16g.

Bromine ... 8.5 c.c.

16 g. of succinimide is dissolved in a mixture of 6.4 g sodium hydroxide, 40 c.c. water and 30 g crushed ice. The flask is cooled in an ice bath and 8.5 c.c. of bromine is added all at one to the vigorously stirred mixture. Stirring is continued for 1-2 minutes after which the precipitate is collected by filtration and is washed with ice water, till the washings are free of bromine. The precipitate is dried at  $40^{\circ}$ . Yield, 20g.



(c) 1-BROMO-2-BROMOMETHYL NAPHTHALENE

1-Bromo-2-methylnaphthalene ... 21g.

N-Bromosuccinimide ... 16g.

Benzoyl peroxide ... 0.1g.

A mixture of 21g. of 1-bromo-2-methylnaphthalene, 16g. of N-bromosuccinimide, 0.1 g of benzoyl peroxide in 25 c.c. of carbon tetrachloride is refluxed for 3 hours. Another 25 c.c. of carbon tetrachloride is then added and the mixture is filtered. The solid residue is washed several times with carbon tetrachloride. The combined filtrate is concentrated to about 10 c.c. and cooled. The product which separates is filtered and melts at 104-105. Yield, 22g.



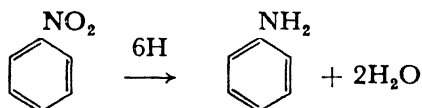
### Preparation 41

#### ANILINE

Nitrobenzene	... 20 g. (17 c.c.)
Granulated tin	... 40 g.
Concentrated hydrochloric acid	... 100 c.c.

The tin is melted in a basin and poured into a flat sand tray, to convert it into feathery tin in which form it is more readily acted on. The tin and the nitrobenzene are introduced into a litre round-bottom flask fitted with a long air-condenser. Hydrochloric acid is added in 10 c.c. portions, cooling the flask under the tap when the reaction becomes violent. The entire quantity of acid is added in about half an hour. The flask is shaken well after each addition and finally heated on a water-bath for an hour or more until no odour of nitrobenzene is perceived. The flask is cooled, the contents diluted with 50 c.c. of water and then a strong solution of commercial caustic soda (150 g. in 200 c.c. water) added a little at a time while cooling under the tap until the stannic hydroxide which is first precipitated dissolves in excess and the solution is strongly alkaline. The aniline that separates is recovered by steam distillation which is continued till no turbidity is seen in the condensing drops. The distillate which is collected in a litre flask is saturated with common salt (25-30 g. for each

100 c.c. of distillate) and extracted thrice with ether in a separating funnel of 500 c.c. capacity, using 50 c.c. of ether each time. The ether extract is dried over caustic soda and filtered into a 250 c.c. distilling flask and the ether removed by distillation on a water-bath. The aniline is transferred to a small distilling flask of 30 c.c. capacity, the original 250 c.c. flask washed with a little dry ether and the washing also added. The ether is removed and the residue distilled using an air-condenser, the portion boiling between  $180-183^{\circ}$  being collected. It is a colourless, highly refractive, oily liquid which gradually darkens ; b.p.  $184.4^{\circ}$  ; sp. gr.  $1.022^{20^{\circ}}$ . Yield, about 12 g.



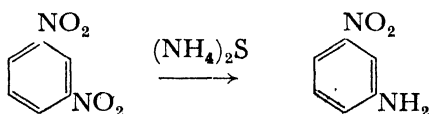
### Preparation 42

#### *m*-NITRANILINE

<i>m</i> -Dinitrobenzene	... 10 g.
Alcohol (rectified spirits)	... 30 g. (38 c.c.)
Ammonia (concentrated)	... 5 g. (sp.gr. 0.88, 6 c.c.)

The crude dinitrobenzene is powdered and weighed into a 100 c.c. conical flask, and dissolved in hot alcohol. The solution is cooled and the ammonia added. The flask is stoppered and weighed along with the tube used for leading in hydrogen sulphide on a rough balance. The mixture is saturated with hydrogen sulphide while cooling by immersion in cold water for about an hour. The hydrogen sulphide is washed by passing the gas through a washing bottle containing water. The flask is then heated under reflux on a water-bath for about 15 minutes, cooled to room temperature and hydrogen sulphide passed once again. This process is repeated till there is a gain in weight of 6 g. The liquid is now poured into cold water (150 c.c.). The precipitate which is a mixture of *m*-nitraniline and sulphur is filtered and washed

with cold water (15 c.c.). The product is extracted thrice by warming with hot dilute hydrochloric acid (10 to 15 c.c.) in a flask and the extract filtered. A few drops of the filtrate are treated in a test tube with ammonia to see if the extraction is complete. The combined filtrate is concentrated to half the bulk and treated with a slight excess of concentrated ammonia to precipitate completely the *m*-nitraniline. The nitraniline is filtered after cooling and recrystallised from boiling water (200 c.c. approximately). It separates in fine yellow needles, m.p.  $112^{\circ}$ . Yield, 5 g.



### Alternative

<i>m</i> -Dinitrobenzene	... 10 g.
Sodium sulphide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ )	... 2.5 g.
Flowers of sulphur	... 5 g.

**Preparation of sodium sulphide.** If sodium sulphide is not available, it can be prepared by dissolving 8 g. of sodium hydroxide in 30 c.c. of water, dividing the solution into two equal parts, saturating one portion with hydrogen sulphide and adding the remainder of the alkali. The flowers of sulphur are dissolved in the sodium sulphide.

10 g. of *m*-dinitrobenzene are powdered and suspended in 75 c.c. of water contained in a 250 c.c. beaker which is heated on a water-bath kept nearly boiling. The contents are stirred by a mechanical stirrer and the sodium sulphide solution with the sulphur dissolved in it, added from a dropping funnel in the course of about ten minutes. To test whether the reaction is complete, a drop of the solution is placed on a filter paper and touched with ferrous or copper sulphate solution. If the black stain persists for a few seconds, the reduction is over and the mixture is cooled to precipitate the nitraniline which is purified as described. It is recrystallised from hot water. Yield, 5 g.

**Preparation 43****BENZIDINE****(a) Hydrazobenzene**

Nitrobenzene	... 25 g.
Zinc dust	... 35 g.
Sodium hydroxide	... 42 g.

A solution of 25 g. nitrobenzene in 250 c.c. methyl alcohol is kept in a 1-litre three-necked flask fitted with a mercury-sealed stirrer and double surface reflux condenser. A solution of 42 g. sodium hydroxide in 100 c.c. of water is then added followed by 35 g. of zinc dust. The stirrer is set in motion and the flask heated on a water-bath. The solution gradually turns red and finally becomes pale yellow (nearly 10 hours). If the colour is not completely discharged, a further 10 g. of zinc dust is added and the stirring continued under reflux for 2-3 hours longer. The hot solution is then filtered through a preheated Büchner funnel and the residue is washed with a little hot methanol. The filtrate is cooled in a freezing mixture for 1 hour and the colourless crystals of hydrazobenzene collected by filtration, and washed with 50 per cent methanol containing sulphurous acid. Yield, 7 g. ; m.p. 125°.

Hydrazobenzene is rapidly oxidized in air and all operations involving filtration should be carried out rapidly without drawing air through it unnecessarily. About 6 g. of impure hydrazobenzene may be recovered from the filtrate by distilling off the methyl alcohol.

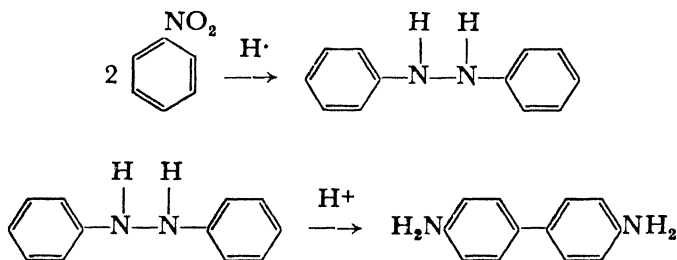
**(b) Benzidine**

Hydrazobenzene	... 9.5 g.
Hydrochloric Acid (1:1)	... 120 c.c.
Ether	... 150 c.c.

9.5 g. of the hydrazobenzene is dissolved in about 100 c.c. ether and the ether solution is added from a separating funnel to 100 c.c. of ice cold dilute hydrochloric acid (1:1) contained in a conical flask with mechanical stirring. Benzidine hydrochloride separates out. After all the hydrazobenzene has been introduced, concentrated hydrochloric acid (50 c.c.) is added and the reaction mixture is allowed to stand for half an hour in ice water. The benzidine hydrochloride is then filtered at the pump, washed

with 20 c.c. of dilute hydrochloric acid and then thrice with 20 c.c. portions of ether to dissolve unchanged hydrazobenzene.

The crude hydrochloride is dissolved in about 200 c.c. water, filtered to remove impurities and cooled rapidly to about 20°. The solution is then passed with stirring into a mixture of 150 g. of crushed ice and 50 c.c. of 10% solution of sodium hydroxide contained in a litre beaker. The precipitated benzidine is filtered off, washed with water and recrystallised from alcohol; m.p. 123, yield, 5 g.



### Preparation 44

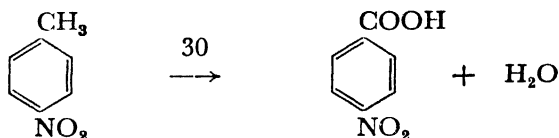
ETHYL-*p*-AMINO BENZOATE  
 ("Anæsthesine hydrochloride")

#### (a) *p*-Nitrobenzoic acid

<i>p</i> -Nitrotoluene	... 23 g.
Sodium dichromate (crystals)	... 68 g. (in 150 c.c. water)
Conc. sulphuric acid	... 170 g. (90 c.c.)

In a bolt-head flask of one litre capacity 150 c.c. of water are measured and the dichromate dissolved in it. The nitro compound is then added and the mixture stirred mechanically while the sulphuric acid is added in drops from a dropping funnel. The heat of dilution melts the nitrotoluene and a vigorous oxidation takes place. Towards the end (about 3 hours) sulphuric acid is added very slowly. When the reaction has subsided, the mixture is

boiled for half an hour. After cooling, 200 c.c. of water are added and the product filtered on glass wool and washed with water. The crude acid is agitated with 100 c.c. of dilute sulphuric acid (N) and warmed. It is filtered and purified by dissolving in a slight excess of 5% caustic soda, filtered again from the unchanged nitrotoluene and chromic hydroxide and acidified with dilute sulphuric acid. It is better to add the alkaline solution to the acid than to reverse the process. The precipitated acid is filtered and washed with water. A sample may be recrystallised from benzene, m.p.  $242^{\circ}$ . Yield, 24 g.



(b) ***p*-Aminobenzoic acid**

<i>p</i> -Nitrobenzoic acid	... 17 g.
Ferrous sulphate	... 200 g.
Water	... 50 c.c.
Ammonia (880)	... 60 c.c.
	(diluted with 40 c.c. water).

Ferrous sulphate crystals washed free from any basic ferric sulphate are dissolved in 400 c.c. of water in a litre porcelain beaker. The solution is heated to boiling and while being vigorously stirred by a mechanical stirrer, the nitrobenzoic acid dissolved in the diluted ammonia is continuously added from a dropping funnel in drops. The boiling solution turns black and turbid. Liquor ammonia is added now and then to keep the liquid slightly alkaline. When all the acid has been added (45 minutes) the stirring and boiling is continued for another ten minutes and the precipitate of ferric hydroxide is filtered off and washed well with water. The combined filtrate is concentrated to about half the bulk, cooled and filtered. The filtrate is carefully acidified with

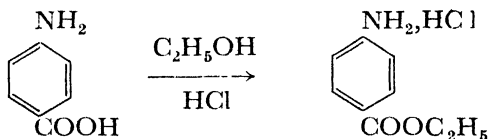


dilute acetic acid (8.5 c.c. of 4N nearly). The precipitated aminobenzoic acid is filtered off, washed with a few c.c. of water and dried. A further quantity of the substance is obtained on concentrating the mother liquor. It is recrystallised from water; m.p. 187°. Yield, 7-8 g.

(c) **Esterification of the acid**

<i>p</i> -Aminobenzoic acid	... 7.5 g.
Alcohol (absolute)	... 43 c.c.

The acid is dissolved in alcohol and saturated with dry hydrogen chloride in the cold (0°). Then the solution is refluxed for an hour and cooled. Crystals of the ester hydrochloride are obtained. These are filtered and recrystallised from alcohol; m.p. 204°. Yield, 7 g.



### Preparation 45

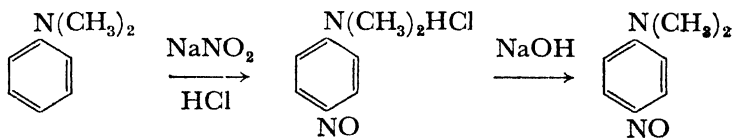
#### *p*-NITROSODIMETHYLANILINE

Dimethylaniline	... 7.5 c.c.
Concentrated hydrochloric acid	... 25 c.c. (dilute with 25 c.c. of water)
Sodium nitrite	... 4.5 g. (in 10 c.c. of water)

***p*-Nitrosodimethylaniline hydrochloride.** The hydrochloric acid diluted with an equal volume of water is taken in a 250 c.c. beaker and the tertiary base dissolved in it. The solution is cooled in a freezing mixture of ice and salt (temperature 0-2°C.) and the sodium nitrite solution is added in lots of 1 c.c. at a time with constant stirring. A drop of the solution is placed on a piece of starch iodide paper to see if the reaction is complete. The mixture is kept for about half an hour in the ice

bath and the yellow crystalline hydrochloride is filtered and washed with ice cold dilute hydrochloric acid, m.p.  $177^{\circ}$ . Yield, 9 g.

**Isolation of the free base.** The hydrochloride is made into a thin cream with 10-15 c.c. of water and transferred to a separating funnel of about 300 c.c. capacity. A ten percent solution of sodium carbonate or sodium hydroxide is added with stirring, till the entire mass becomes bright green. The base is extracted with 25 c.c. of benzene twice and the extract dried over anhydrous potassium carbonate for about 15 minutes. Nearly half the benzene is removed by distillation on a water-bath and the hot solution of the base is transferred to dry porcelain basin for crystallisation. Brilliant green leaflets are obtained and they crumble to a fine green crystalline powder after filtration and drying, m.p.  $85^{\circ}$ . Yield, 7.8 g.



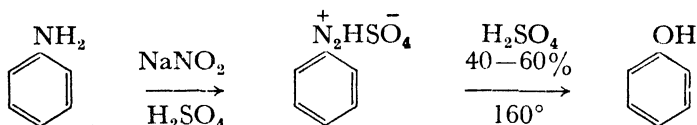
## Preparation 46

### PHENOL

Aniline	... 15 g.
Concentrated sulphuric acid	... 20 c.c.
Sodium nitrite	... 12 g. (in 30 c.c. water)

20 c.c. of concentrated sulphuric acid are diluted with 75 c.c. of water in a 250 c.c. beaker and the aniline added with stirring while the mixture is still hot. The beaker is cooled in ice and the sodium nitrite solution added drop by drop from a dropping funnel, the end of the dropping funnel dipping under the surface of the liquid. The mixture is stirred well with a glass rod during the addition of the nitrite which is continued till a drop of the solution placed on starch iodide paper produces a blue colour

showing that there is an excess of nitrite. The solution is then transferred to a 1-litre round-bottom flask and heated gently on a water-bath with an air-condenser. A vigorous reaction takes place with evolution of nitrogen and formation of phenol. When the reaction has subsided, the product is distilled in a current of steam till a few drops of the distillate tested with a solution of ferric chloride, fail to give any colour. The distillate (about 300 c.c.) is saturated with sodium chloride and extracted thrice with ether using 50 c.c. each time. The combined ether extract is dried over anhydrous sodium sulphate or magnesium sulphate for about an hour in a separating funnel. The ether is distilled off on the water-bath and the phenol distilled from a small distilling flask (25 c.c.) using an air-condenser. The fraction boiling between 180-183° is collected. It freezes to a colourless, crystalline solid, m.p. 41° ; b.p. 182°. Yield, 10 g.



### Preparation 47

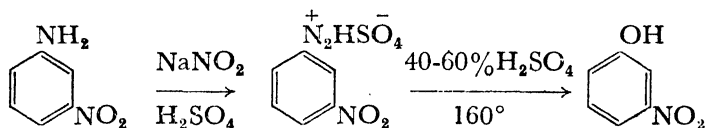
#### *m*-NITROPHENOL

<i>m</i> -Nitraniline	... 12 g.
Sodium nitrite	... 6 g. in 14 c.c. water)
Con. sulphuric acid	... 18 c.c. (in 25 c.c. water.)

18 c.c. of concentrated sulphuric acid are cautiously diluted with 25 c.c. of water in a 450 c.c. beaker and 12 g. of finely powdered *m*-nitraniline is added with stirring to the sulphuric acid. Then 40 to 50 g. of crushed ice are added and the mixture stirred until the *m*-nitraniline has been converted into the sulphate and a homogenous paste results. The mass is cooled to between 0-5° by placing the beaker in a freezing mixture. A solution of 6 g. of sodium nitrite in 14 c.c. water is then added over a period of 10 minutes until a test portion gives a permanent immediate

colour with potassium iodide-starch paper. Care is taken to see that the temperature does not rise above 5 to 7° during diazotisation. The stirring is continued for 5 to 10 minutes and the mixture allowed to stand for 5 minutes ; some *m*-nitrophenyl-diazonium sulphate may separate. The supernatant liquid is decanted from the solid as far as possible.

While the diazotisation is in progress, 55 c.c. of concentrated sulphuric acid are added carefully to 50 c.c. of water in a 500 c.c. round-bottom flask. The mixture is heated to boiling. The supernatant liquid (diazonium solution) is added from a separating funnel supported over the flask at such a rate that the mixture is maintained at the boiling point. The residual damp solid (or suspension) is then added in small portions. When all the diazonium salt has been introduced the boiling is continued for a further 5 minutes and the mixture is poured into a 500 c.c. beaker cooled in ice water and stirred vigorously. Crystals of *m*-nitrophenol separate. After filtration and washing with a small quantity of water, recrystallisation is effected from dilute hydrochloric acid, giving light yellow crystals, m.p. 96°. Yield, 7 g.



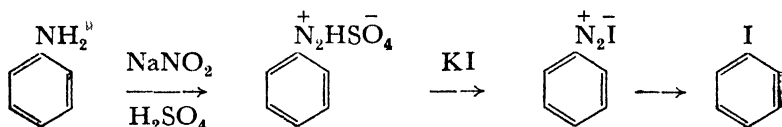
### Preparation 48

#### IODOBENZENE

Aniline	... 10 g.
Con. sulphuric acid	... 12 c.c. (about 21 g.)
Sodium nitrite	... 8 g. (in 20 c.c. water)
Potassium iodide	... 22 g.

The aniline is diazotised as before and the diazo solution is poured into a litre flask. The potassium iodide dissolved in 50 c.c.

of water is then added and the flask kept on a water-bath heated to about  $80^{\circ}$  with an air-condenser till the evolution of nitrogen ceases. Iodobenzene separates as a dark heavy oil and is distilled in steam. The distillate is extracted thrice with ether (50, 40 and 30 c.c.) and the ether extract washed with water at first and then with dilute sodium hydroxide solution till all free iodine is removed. The ether extract is dried for about 15 minutes over calcium chloride after which the ether is removed by distillation on a water-bath. The iodobenzene is then distilled using an air-condenser and the portion boiling at  $188-190^{\circ}$  collected. It is a heavy yellow liquid, b.p.  $188.6^{\circ}$ ; sp. gr.  $1.832^{20^{\circ}}$ . Yield, 18 g.



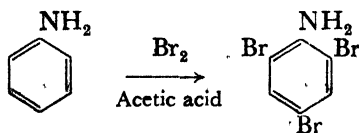
### Preparation 49

#### 1 : 3 : 5-TRIBROMOBENZENE

##### (1) 2 : 4 : 6-Tribromoaniline.

Aniline	... 5 c.c.
Bromine	... 8.5 c.c.

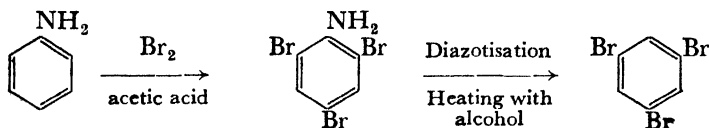
A solution of 5 c.c. aniline in 20 c.c. of glacial acetic acid is cooled in an ice bath and stirred mechanically. The bromine (8.5 c.c.) is run in from a separating funnel dropwise. At the end, if the pasty reaction mass is not coloured yellow, a little more bromine is added. The mass is then poured into 200 c.c. water, filtered, washed well with water and dried. Yield, 16 g. On crystallisation from alcohol the tribromoaniline melts at  $120^{\circ}$ .



(2) 1 : 3 : 5-*Tribromobenzene*.

2 : 4 : 6-Tribromoaniline	... 10 g.
Rectified spirits	... 60 c.c.
Benzene	... 15 c.c.
Concentrated sulphuric acid	... 3.5 c.c.
Sodium nitrite (powdered)	... 3.5 g.

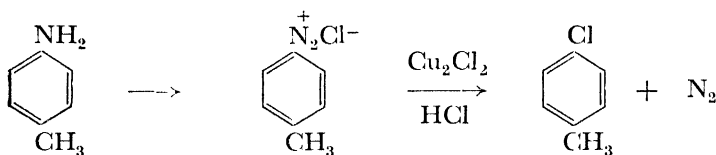
10 g. of 2 : 4 : 6-tribromoaniline are dissolved in 60 c.c. of rectified spirits and 15 c.c. of benzene by heating on a water bath. 3.5 c.c. of concentrated sulphuric acid are added to the hot solution with stirring. A reflux condenser is attached and the mixture is heated on a water bath till the clear solution starts boiling. The condenser is then detached, the flask is removed from the water bath and 3.5 g. of powdered sodium nitrite is added in approximately two equal portions, fitting the condenser after each addition and shaking vigorously. A vigorous exothermic reaction sets in after each addition. The flask is then heated under reflux on a boiling water bath as long as gas is evolved, shaking from time to time. The solution is allowed to cool to room temperature and then cooled in ice. The mixture of tribromobenzene and sodium sulphate which separates is filtered and repeatedly washed with water to remove all sodium sulphate. Purification is effected by dissolving in 120 c.c. of glacial acetic acid and 30 c.c. water by heating to boiling. The solution is decolourised by addition of norit and filtered through a hot water funnel. The crystals from the filtrate, after cooling down to room temperature are collected on a Büchner funnel and washed with a few c.c. of cold rectified spirits. The pure product melts at 122°. Yield, 6.5 g.

**Preparation 50***p*-CHLOROBENZOIC ACID(a) *p*-Chlorotoluene

<i>p</i> -Toluidine	... 15 g.
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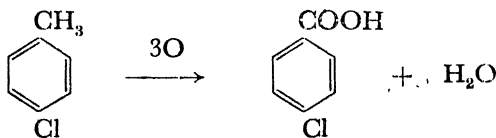
Sodium nitrite (in 30 c.c. water)	... 12 g.
Concentrated hydrochloric acid	... 36 c.c.
	(in 25 c.c. water)
Cupric chloride (for cuprous chloride preparation)	... 31 g.

The *p*-toluidine is dissolved in the hydrochloric acid, cooled and diazotised as usual in ice-cold solution. The diazo-solution is slowly poured into a nearly boiling solution of the cuprous chloride contained in a litre roundbottom flask. The mixture is kept hot on a boiling water-bath for half an hour and then steam distilled. The oily distillate is washed with dilute sodium hydroxide, then with water and finally dried over calcium chloride. The liquid is distilled, the portion coming over between 160-164° being collected. It is a colourless liquid ; b.p. 162° ; sp. gr. 1.071<sup>18°</sup>. Yield, 11 g.



(b) **Oxidation of *p*-chlorotoluene to *p*-chlorobenzoic acid**

4 g. of the chlorotoluene are oxidized with potassium permanganate as usual in a 300 c.c. round-bottom flask fitted with a reflux condenser, the contents of the flask being kept on the brisk boil continuously. The oxidation is a slow process and takes about 6 hours. When all the oil has practically disappeared and there is a permanent pink colour, the flask is cooled and the acid liberated by passing sulphur dioxide. The chlorobenzoic acid is precipitated on cooling and is recrystallised from dilute alcohol, m.p. 242°.



## Preparation 51

### PHENYLHYDRAZINE

Aniline	... 11 g.
Con. hydrochloric acid	... 38 c.c. (diluted with about 50 c.c. of water)
Sodium nitrite	... 10.5 g. (dissolved in 20 c.c. of water.)
Sodium sulphite	
Anhydrous sodium carbonate.	... 12 g.

*Note :* To prepare the sodium sulphite, 35 g. of anhydrous sodium carbonate are dissolved in 50 c.c. of water. The solution is divided into two equal parts, one part is saturated with sulphur dioxide and the second part then added.

The sodium carbonate is added to the prepared sodium sulphite solution which is kept in a litre beaker well cooled in ice. Aniline is diazotised as usual and the diazo solution is added gradually with constant stirring to the sulphite solution. A deep orange crystalline precipitate is obtained. The mixture is kept stirred for another fifteen minutes and saturated at room temperature (about 30°) with sulphur dioxide to reduce the diazobenzene sulphonate. After saturation, it is warmed to about 70° by heating on a water-bath and filtered. The filtrate is treated with 100 c.c. of concentrated hydrochloric acid, when the phenylhydrazine hydrochloride separates slowly. The crystallisation is completed by leaving it overnight, after which it is filtered. The hydrochloride is suspended in water and rendered alkaline with caustic soda solution. The free base liberated as a red oil is extracted twice with 75 c.c. of benzene. The benzene solution is dried over caustic soda pellets and the benzene removed by distillation on water-bath. The residue is distilled under reduced pressure, the portion boiling below 100° being rejected. Phenylhydrazine boils at 140° under 60 mm. pressure. The portion boiling steadily under the indicated pressure is collected. It is a light yellow liquid when freshly distilled; b.p. 243.5°; sp. gr. 1.098<sup>20°</sup>. Yield, 10 to 11 g.

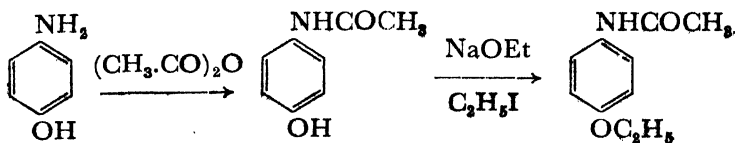


**Preparation 52****PHENACETIN**

<i>p</i> -Aminophenol	... 11 g.
Acetic anhydride	... 12 c.c.
Sodium metal	... 1.6g.
Absolute alcohol	... 40 c.c.
Ethyl Iodide	... 8 c.c. (15 g.)

11 g. of *p*-aminophenol are suspended in 30 c.c. of water contained in a 250 c.c. of beaker or conical flask, and to this suspension is added 12 c.c. of acetic anhydride with vigorous stirring or shaking. The mixture is then warmed on a water bath. The solid dissolves. After 10 minutes, the solid acetyl derivative is filtered after cooling, washed with a little cold water, recrystallised from hot water (about 75 c.c.) and dried upon filter paper in the air. The yield of *p*-acetylaminophenol, m.p. 169° is 14 g.

To 40 c.c. of absolute alcohol in a 250 c.c. round-bottom flask fitted with a reflux condenser, 1.6 g. of sodium are added. Vigorous reaction starts. If by the time the reaction subsides, all the sodium has not disappeared, the flask is warmed on a water-bath until the solution is complete. The mixture is cooled and 10 g. of *p*-acetylaminophenol are added. 15 g. (8 c.c.) of ethyl iodide are added slowly through the condenser and the mixture is refluxed for about 45-60 minutes. 100 c.c. of water are then added through the condenser at such a rate that the crystalline product does not separate; if crystals do separate, the mixture is refluxed until the crystals redissolve. The flask is then cooled in an ice bath. The crude phenacetin which separates is filtered and washed with a little cold water. The crude product is dissolved in 80 c.c. of rectified spirits, refluxed after addition of norit and filtered. The clear solution is treated with 125 c.c. of hot water and allowed to cool. The pure phenacetin is collected by filtration and dried. It melts at 136°. Yield, 9.5 g.



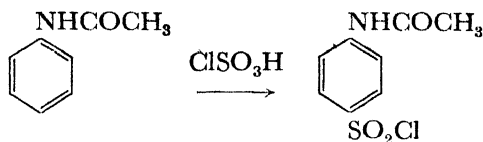
**Preparation 53*****p*-AMINOBENZENESULPHONAMIDE (SULPHANILAMIDE)**

Acetanilide	... 15 g.
Chlorosulphonic acid (freshly distilled)	... 38 c.c.

The preparation is carried out in three stages.

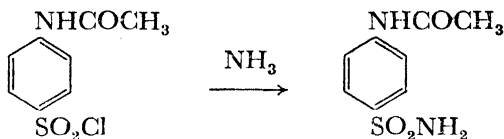
**1. *p*-acetaminobenzenesulphonylchloride**

The chlorosulphonic acid is introduced into a 250 c.c. three-necked flask fitted with a reflux condenser, and a mechanical stirrer with mercury seal. The flask is kept cold by surrounding it with ice in a trough. The dry acetanilide is then added through the third neck removing the cork when necessary, in small amounts, while the contents are kept stirred. The condenser top is connected to a gas trap to absorb the hydrogen chloride liberated. After the addition is over, the flask is warmed on a water-bath at 60° to complete the reaction, the time taken being about 15 minutes. The flask is cooled under the tap, the stirrer, condenser etc. dismantled, and the syrupy liquid is poured in a thin stream with stirring into a 500 c.c. beaker containing crushed ice, the beaker itself being surrounded by ice in a trough. The flask is rinsed with a little ice water and the rinsings added to the beaker. The granular white solid is filtered on a Buchner funnel, washed with ice-cold water, pressed and drained well. The crude product (about 20 g.) is immediately used in the next stage.

**2. *p*-Acetaminobenzenesulphonamide**

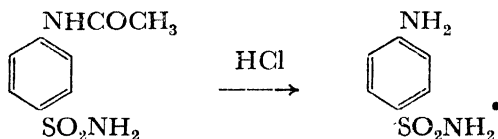
The crude *p*-acetaminobenzenesulphonyl chloride is transferred to a 500 c.c. round-bottom flask. 4.5 c.c. of liquor ammonia (sp. gr. 0.88) and 45 c.c. of water are then added to the flask. The contents of the flask are thoroughly mixed and the mixture is

heated with occasional swirling to just below the boiling point for about 15 minutes. The sulphonylchloride is transformed into a paste of sulphonamide. The pasty suspension is cooled in ice and filtered on a Buchner funnel and drained thoroughly. Yield, 14 g.



### 3. Hydrolysis of *p*-acetaminobenzenesulphonamide

The product obtained above is transferred to a 250 c.c. round-bottom bolt head flask, 8 c.c. of concentrated hydrochloric acid and 30 c.c. of water are added and the mixture is boiled gently under reflux for 30-40 minutes. If the solution, when cooled to room temperature deposits any solid amide, the hydrolysis should be continued further by heating for some more time. The cooled solution is heated with 1 to 2 g. of norit, heated to boiling and filtered through a fluted filter paper. The filtrate (a solution of sulphanilamide hydrochloride) is transferred to a litre beaker and carefully neutralised with solid sodium bicarbonate which is added in small quantities at a time with stirring. The solution is tested finally with litmus to see that it is neutral. It is then cooled in ice, and the precipitated sulphanilamide filtered and crystallised from alcohol. M.p. 151-163°; Yield, 10-11 g.



*Note.*—Chlorosulphonic acid is very corrosive and reacts with water violently and hence has to be handled with care. If the

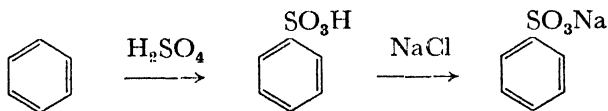
sample is impure or coloured it is best purified by distillation in an all-glass apparatus. The fraction boiling between  $148-150^{\circ}$  is collected, taking care to guard it from moisture.

### Preparation 54

#### SODIUM BENZENESULPHONATE

Benzene	... 20 g. (23 c.c.)
Fuming sulphuric acid (5-7% $\text{SO}_3$ )	... 85 g. (45 c.c.)

The sulphuric acid is taken in a 250 c.c. round-bottom flask fitted with a reflux condenser and the benzene added slowly from a dropping funnel with continued shaking, taking care not to add fresh benzene until the first quantity added is completely dissolved. During the addition, the flask is cooled in water and the temperature not allowed to rise above  $50-60^{\circ}$ . After about twenty minutes during which time the benzene dissolves completely, the reaction mixture is added very slowly to 200 c.c. of a saturated and filtered solution of sodium chloride contained in a beaker surrounded by ice water. If the sides of the beaker are rubbed with a glass rod, the sodium salt crystallises in plates. A purer substance is obtained by recrystallisation from alcohol. For every gram of the salt about 20 c.c. of alcohol are necessary. Purification is best effected by using the Soxhlet extractor which saves a considerable amount of alcohol, 100 c.c. being quite sufficient. The salt comes out in colourless plates which melt very high, above  $410^{\circ}$ . Yield, 19 g.

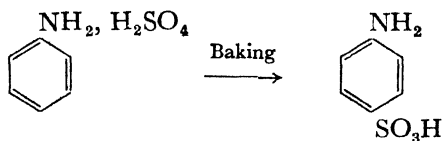


### Preparation 55

#### SULPHANILIC ACID

Aniline (freshly distilled)	... 14 g. (14 c.c.)
Concentrated sulphuric acid	... 40 g. (22 c.c.)

The aniline is measured into a 250 c.c. round-bottom flask and the sulphuric acid carefully added in 2 c.c. lots, cooling under the tap after each addition. Solid aniline sulphate separates. The flask is fitted with an air-condenser and heated in an oil-bath at 180-190° for 4-5 hours. Two drops of the reaction mixture are poured into 7 c.c. of sodium hydroxide (bench reagent) and if no oily drops separate, the reaction is regarded as complete. The heating is stopped at this stage, the reaction mixture is cooled, and poured carefully with stirring, into 100 c.c. of cold water. The crude product separates as a grey crystalline mass. It is filtered, washed with 25 c.c. of cold water and suspended in about 250 c.c. of water contained in a large beaker. Two grams of norit are added and the contents of the beaker are boiled for about 10 minutes. The solution is filtered using a hot-water funnel and the filtrate left to crystallise. It crystallises with two molecules of water. No definite m.p. Yield, 12-14 g.



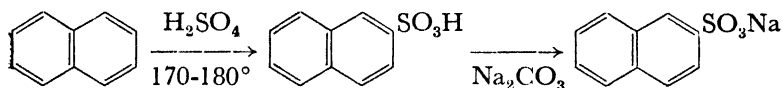
### Preparation 56

#### SODIUM $\beta$ -NAPHTHALENESULPHONATE

Naphthalene	... 20 g.
Concentrated sulphuric acid	... 25 g.

The powdered naphthalene and the sulphuric acid are heated in a round-bottom flask at 170-180° in a metal or oil bath for six hours. The cooled mass is poured with stirring into a basin containing 500 c.c. of water and the unchanged naphthalene is filtered. The filtrate is heated to boiling and neutralised by the addition of chalk or slaked lime in the form of a thick cream. The precipitated calcium sulphate is filtered hot and the residue washed with a little water. The combined filtrate and washings are concentrated by evaporation until a sample crystallises on cooling. Saturated

sodium carbonate solution is added to the hot liquid till no further precipitation occurs. The precipitated chalk is filtered and the filtrate is evaporated almost to dryness, when the sodium salt crystallises out. The salt is filtered and dried in a basin on a water-bath. Yield, 24 g.



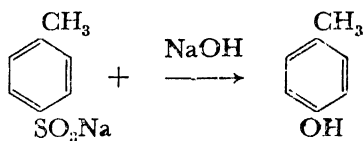
### Preparation 57

#### *p*-CRESOL FROM SODIUM *p*-TOLUENESULPHONATE

Sodium <i>p</i> -Toluenesulphonate	... 25 g.
Potassium hydroxide	... 75 g.
Sulphuric acid (concentrated)	... 35 c.c. (diluted with 80 c.c. water)

The potassium hydroxide is melted carefully in a nickel basin of 10 cm. diameter. The fused mass is kept stirred by a closed glass tube containing a little mercury into which the bulb of a thermometer is dipping. This is to prevent the hot alkali from acting on the glass of the thermometer. 25 g. of the sulphonate are added in lots of 2 g. with stirring. The temperature is maintained between 230-270° during the addition which should require about 20 minutes. The temperature is then raised to 300°. If there is a tendency for the mixture to froth over, the burner is temporarily removed. The temperature is then gradually raised to about 330° after the frothing disappears, and when the mixture is uniform it is poured into a clean sand tray. The solid is dissolved in water (about 300 c.c.) and treated with sulphuric acid till there is a smell of sulphur dioxide. The hot solution is steam distilled till a sample of the distillate does not react with bromine water. The distillate is saturated with salt and extracted with ether thrice and the ether extract dried over sodium sulphate or anhydrous magnesium sulphate. The ether is removed by distillation and the cresol distilled, collecting the portion coming over between

195-200°. It is obtained as a colourless liquid, b.p. 201°. Yield, 11 g.

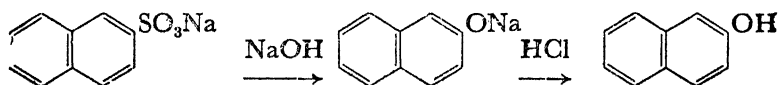


### Preparation 58

#### $\beta$ -NAPHTHOL FROM SODIUM $\beta$ -NAPHTHALENESULPHONATE

Sodium $\beta$ -Naphthalenesulphonate	... 20 g.
Caustic soda	... 60 g.
Water	... 2 c.c.

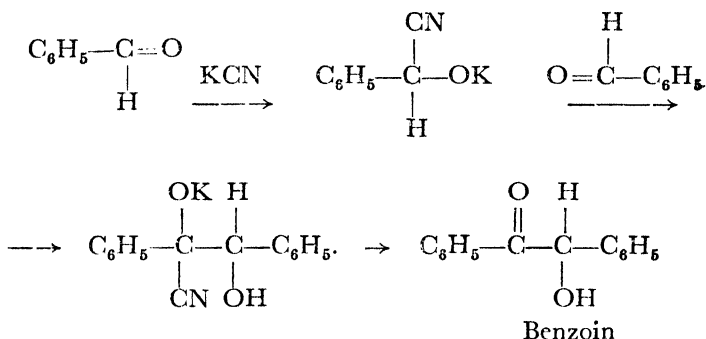
The caustic soda and water are heated in a nickel crucible or basin carefully till a temperature of about 280° is reached. The molten mass is stirred by a closed tube containing a little mercury into which the thermometer is dipping. The powdered sodium salt is added a little at a time and the temperature gradually raised to 300-320°. The mass shows a tendency to froth up and assumes a light yellow colour. The mass is heated at this temperature for about 10 minutes. The completion of the reaction is shown by the separation of two layers and the darkening of the colour. The melt is poured into a clean tray, pulverised when cold, dissolved in the minimum amount of water (100 c.c.) and acidified with (1 : 1) hydrochloric acid. The precipitate of  $\beta$ -naphthol is filtered, washed with water and recrystallised from hot water. It crystallises in colourless leaflets, m.p. 122°. Yield, 10 g.



**Preparation 59****BENZOIN**

Benzaldehyde	... 20 g.
Potassium cyanide	... 4 g. (in 15 c.c. water)
Rectified spirits	... 40 c.c.

The mixture of benzaldehyde, potassium cyanide solution and alcohol is refluxed in a 250 c.c. round-bottom flask for about an hour. On cooling, benzoin separates as a crystalline mass which is filtered and washed with a little alcohol. About 2 g. are recrystallised from alcohol and the rest used for the succeeding experiment. It crystallises in colourless prisms, m.p. 133°. Yield, 16 g.

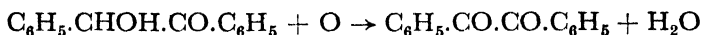
**Preparation 60****BENZIL**

Benzoin	... 15 g.
Concentrated Nitric acid	... 25 c.c.
(sp. gr. = 1.42)	

The benzoin and nitric acid are mixed in a 200 c.c. flask and heated on the water-bath with an air-condenser, the flask being occasionally shaken. A vigorous reaction takes place with evolution of copious nitrous fumes and the crystals of benzoin are converted into a yellow oil. After heating for two hours, the product is poured into cold water with vigorous stirring, the crystalline mass is filtered, washed with cold water and recrystallised



from alcohol. It crystallises in yellow prisms, m.p. 95°. Yield, 10-12 g.



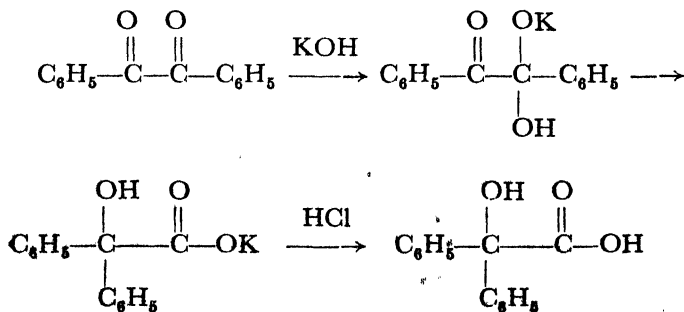
[The experiment should be done in a fume cup-board.]

### Preparation 61

#### BENZILIC ACID

Benzil	... 10 g.
Caustic potash	... 10 g. (in 20 c.c. water)
Rectified spirits	... 27 c.c.

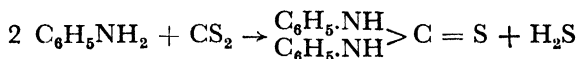
The benzil is dissolved in alcohol in a 250 c.c. round-bottom flask and the caustic potash solution added. The mixture is refluxed for about 12 minutes on a boiling water-bath, the contents are poured into a beaker and left overnight. The potassium salt of benzilic acid is filtered and washed with a little alcohol. The mother liquor on evaporation yields a little more of the salt. The crystals are dissolved in half a litre of water, the solution is filtered, boiled and acidified with hot dilute sulphuric acid till acid to congo red paper. The acid can be crystallised from benzene or from hot water with the addition of a little animal charcoal. It crystallises in colourless needles, m.p. 150°. Yield, 10 g.



**Preparation 62****THIOCARBANILIDE**

Carbon disulphide	... 25 g.
Aniline	... 20 g.
Absolute alcohol	... 30 c.c.
Caustic potash (powdered)	... 5 g.

The aniline, carbon disulphide and alcohol are taken in a 250 c.c. round-bottom flask fitted with a long reflux condenser and the powdered caustic potash slowly added. The mixture is refluxed for 3 hours on a water-bath. The unreacted carbon disulphide and alcohol are then distilled off and the residue washed with water and dilute hydrochloric acid to remove aniline. The solid is filtered, washed with water and dried. A small portion may be recrystallised from alcohol. It crystallises in colourless plates, m.p. 154°. Yield, 16 g.

**Preparation 63****PHENYL ISOTHIOCYANATE**

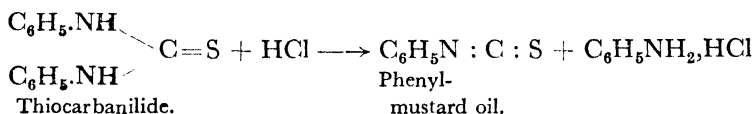
Thiocarbanilide	... 15 g.
Concentrated hydrochloric acid	... 50 c.c.

The thiocarbanilide and hydrochloric acid are boiled under reflux for half an hour. The phenyl isothiocyanate separates as an oil and is recovered by steam distillation or simple distillation, till there is a residue of about 10 c.c. The distillate is extracted with ether, dried over calcium chloride and distilled after removal of ether, the fraction boiling between 218-222° being collected. Since the quantity obtained is small, the distillation may be carried out in a test-tube with side-tube. It is a colourless liquid with a pungent odour. b.p. 218°; sp. gr. 1.135/15°. Yield, 1.5 g.

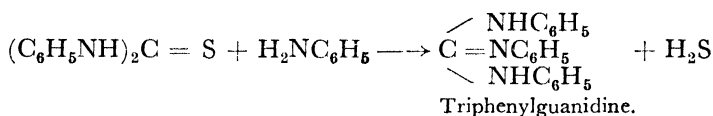
The residue in the flask consists of triphenylguanidine hydrochloride. This is separated after cooling by filtration and dried.

with a little water. The hydrochloride is warmed gently for a few minutes with dilute caustic soda solution. The free base is liberated, filtered, washed with water and recrystallised from alcohol. Colourless needles, m.p. 143°. Yield, 1-2 g.

**Primary reaction :**



**Secondary reaction :**

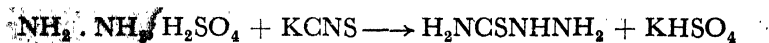


**Preparation 64**

THIOSEMICARBAZIDE

Hydrazine sulphate	... 25 g.
Potassium thiocyanate	... 20 g.
Potassium carbonate	... 13.5 g.

A mixture of 25 g. of hydrazine sulphate and 100 c.c. of water is warmed and 13.5 g. of anhydrous potassium carbonate are added. After addition of 20 g. of potassium thiocyanate the mixture is boiled for a few minutes and treated with 200 c.c. of hot alcohol. The precipitated potassium bisulphate is removed by filtration. The filtrate is concentrated by heating in a porcelain basin with vigorous stirring to a syrupy consistency. The mass is cooled, water is added and the resulting crude thiosemicarbazide is filtered off. The filtrate is evaporated and the above treatment is repeated. After one crystallisation from water, colourless needles m.p. 181-183° are obtained. Yield, 10g.



**Preparation 65****S-BENZYL-*Iso*-THIURONIUM CHLORIDE**

Benzyl chloride	... 16 g.
Thiourea	... 7 g.
Rectified spirits	... 20 c.c.

A mixture of benzyl chloride, thiourea and rectified spirits is placed in a 250 c.c. round bottom flask fitted with a reflux condenser and carefully warmed on a water bath to initiate the reaction which is exothermic and sets in all of a sudden. The flask is raised from the water bath in order to lessen the vigour of the reaction. The thiourea passes into solution. After the vigour of the reaction has subsided, the resulting yellow solution is refluxed for about half an hour and then cooled in ice. White crystals separate. They are filtered on a Büchner funnel and dried in air. On concentration of the mother liquor, a further crop of crystals are obtained. The yield of crude S-benzyl-iso-thiuronium chloride m.p. 145° is 28 g. On crystallisation from N/5 hydrochloric acid, the melting point is raised to 150° although on some occasions, the form m.p. 170° separates.

*Note:*—Benzyl chloride reacts with thiourea in dilute alcoholic solution to give S-benzyl-iso-thiuronium chloride. The compound separates in either of two polymorphic forms, m.p. 150° and 170° (sometimes both) respectively. The former may be converted into the higher m.p. form by dissolving it in alcohol and seeding with crystals of the form m.p. 170°. The lower m.p. form when warmed to 170° gives, after solidification, a m.p. of 175°. Both polymorphic forms give identical derivatives with carboxylic acids and sulphonic acids.

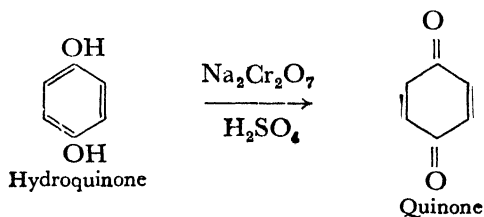
**Preparation 66****QUINONE**

Hydroquinone	... 20 g.
Sodium dichromate	... 15 g.
Sulphuric acid (concentrated)	... 11 g.

20 g. of hydroquinone are dissolved in 200 c.c. of water at 50°. The clear solution is cooled to 10° and then treated slowly

(without allowing the temperature to rise) with 11 g. (6 c.c.) of the sulphuric acid. A saturated solution of sodium dichromate (15 g.) in water is added dropwise with mechanical stirring, to the cold solution of hydroquinone, in the course of about 45 minutes. The temperature rises with addition of the dichromate solution, but care is taken to see that the temperature does not rise above 30°. The stirring is continued for about 10 minutes after the addition is over, and the precipitated quinone is filtered on a Buchner funnel, drained well and freed from water as far as possible by pressing with a stopper while still under suction.

The filtrate is extracted twice with benzene (50 c.c.) to recover any dissolved quinone. The filtered solid is then dissolved (with excess benzene, if necessary) in the benzene extract. The benzene solution is dried over anhydrous calcium chloride, filtered into a dry conical flask and concentrated to a small bulk when yellow needles of quinone separate. The crystals are filtered at the pump and air dried ; m.p. 115-116°. Yield, 15-16 g.



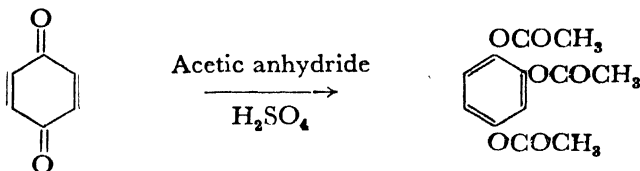
### Preparation 67

#### HYDROXYHYDROQUINONE TRIACETATE

Quinone	... 16 g.
Acetic anhydride	... 48 g.
Concentrated sulphuric acid	... 3.2 g.

3.2 g. of concentrated sulphuric acid is slowly added to 48 g. of acetic anhydride in a 250 c.c. round bottom flask. The finely powdered hydroquinone (16 g.) is then added in small quantities at a time to the well stirred mixture of acetic anhydride and sulphuric acid in the course of about 10 minutes. The temperature is maintained between 40-50° during this addition. When the

addition is over, stirring is continued for about 5 minutes and the contents of the flask are poured over crushed ice in a 500 c.c. beaker. The white granular solid is then filtered at the pump, washed well with water and freed as much as possible from water by suction. The solid is then crystallised from 50 c.c. of rectified spirits; m.p. 96-97°. Yield, 35 g. The triacetoxo benzene is reactive and is stored in a calcium chloride desiccator in an atmosphere of carbon dioxide.

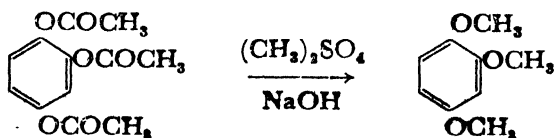


### Preparation 68

#### 1 : 2 : 4-TRIMETHOXYBENZENE

1 : 2 : 4-Triacetoxibenzenes	... 35 g.
Methyl alcohol	... 50 c.c.
Dimethyl sulphate	... 125 c.c.
Sodium hydroxide (flakes)	... 105 g.

35 g. of the triacetate are dissolved in a mixture of 60 c.c. of methyl alcohol and 125 c.c. of dimethyl sulphate in a 500 c.c. round-bottom bolt-head flask. A solution of 105 g. of sodium hydroxide in 105 c.c. of water is then added dropwise in the course of about 2 hours to the contents of the flask with efficient stirring, taking care to maintain the temperature between 25-30° by external cooling of the flask. The stirring is continued for about an hour after addition is over, and then 350 c.c. of water are added. A clear yellow oil separates. The entire alkaline solution is repeatedly extracted with ether. The combined ether extract is dried over anhydrous sodium sulphate. The ether is removed over a water-bath and the oil left behind is purified by distillation. 1 : 2 : 4-trimethoxybenzene is a colourless oil boiling at 247°C. Yield, 15-16 g.



**Preparation 69****THYMOQUINONE**

Thymol	... 20 g.
Alcohol	... 125 c.c.
Conc. Hydrochloric acid	... 125 c.c.
Sodium nitrite	... 18 g.

(a) **Nitroso thymol.** The thymol is dissolved in the requisite amount of alcohol contained in a one litre beaker and the hydrochloric acid added afterwards. The beaker is cooled in ice, the contents are stirred mechanically and the sodium nitrite is added in portions of 3 g. at a time. The solution becomes brown at first and subsequently a green precipitate begins to form. The mixture becomes pasty when about half the sodium nitrite has been added. It is stirred more vigorously and the addition made at longer intervals. The product is transferred to a three litre flask containing two litres of cold water, the mixture well-agitated, and the light yellow fluffy solid filtered and washed thoroughly with cold water. The product is nitrosothymol.

(b) **Amino thymol.** The crude, wet nitrosothymol obtained above is treated with a mixture of 225 c.c. of liquor ammonia (sp. gr. 0.9) and 400 c.c. of water. The brown solution is filtered free of resinous matter and hydrogen sulphide is passed into it. Very soon the brown colour disappears and a white precipitate is formed. The passage of hydrogen sulphide is continued for about ten minutes more, and the free base (aminothymol) filtered at the pump, and washed well with cold water.

(c) **Thymoquinone.** The wet amino-thymol obtained above is immediately dissolved in 27.5 c.c. of concentrated sulphuric acid and the solution diluted to a litre. Sodium nitrite (38 g.) is added to the solution in lots of 5 g., with shaking between consecutive additions. The mixture is heated to 60° on a water-bath for half an hour with occasional shaking, and then distilled in steam, a litre of the distillate being collected. The distillate is cooled in ice and the bright yellow crystals of thymoquinone are filtered and dried on a porous plate; m.p. 45°. Yield, 18.5 g.

**Preparation 70****ANTHRAQUINONE****(a) o-Benzoylbenzoic acid**

Benzene (dry)	... 35 g.
Phthalic anhydride	... 10 g.
Aluminium chloride (anhydrous)	... 18 g.

Into a three-necked 250 c.c. flask fitted with a reflux condenser and a mechanical stirrer (mercury seal), the dry benzene and phthalic anhydride are introduced and resublimed aluminium chloride is added (Fig. 41). The mixture is heated on a water bath to start the reaction and when the reaction becomes vigorous the flask is surrounded by cold water. When the mass becomes viscous, the stirring is stopped and the temperature kept at 70° till hydrogen chloride ceases to be evolved. The stirrer is removed and four times the volume of cold water is added through a dropping funnel a little at a time. Considerable heat is evolved. The mixture is then submitted to steam distillation to remove benzene completely and the residue is boiled for two hours making it alkaline with caustic soda. The precipitated alumina is filtered off and washed with boiling water. The filtrate containing the sodium salt of the acid is acidified with dilute hydrochloric acid and the liberated acid is filtered and recrystallised from water. It comes out in colourless crystals, m.p. 127° (anhyd.), monohydrate, m.p. 94°. Yield, 14 g.

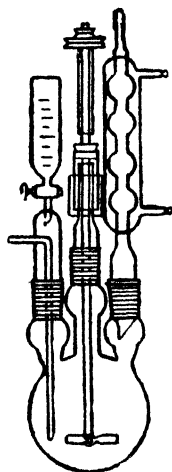
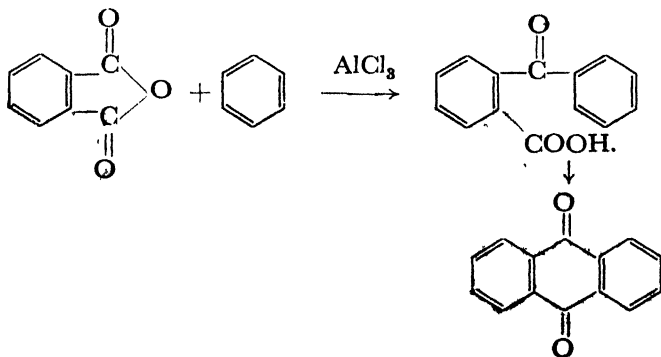


Fig. 42. Three-necked flask with mechanical stirrer, mercury seal, condenser, dropping funnel and leading-in tube.





**(b) Anthraquinone**

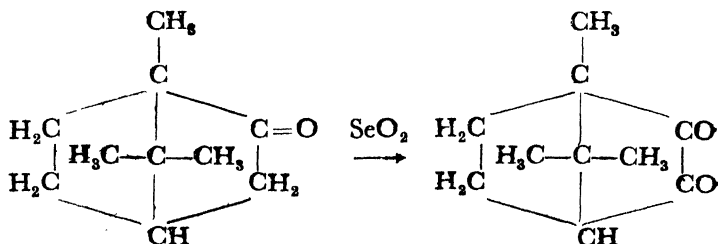
5 g. of o-benzoylbenzoic acid are mixed with 30 g. of concentrated sulphuric acid and heated at  $150^{\circ}$  for an hour in an oil-bath. The mixture is cooled and poured into a beaker containing crushed ice. The precipitated anthraquinone is collected and thoroughly washed with hot water at first and then with warm dilute sodium hydroxide (4N) and finally freed from alkali by washing with warm water. It may be dried in the air oven at  $100-110^{\circ}$  and purified by sublimation at  $250^{\circ}$ . Fine yellow needles, m.p.  $285^{\circ}$ . Yield, 4 g.

**Preparation 71****CAMPHORQUINONE**

Camphor (natural)	... 5 g.
Selenium dioxide	... 6 g.
Acetic anhydride	... 5 c.c.

Finely powdered camphor and acetic anhydride are introduced into a 100 c.c. round bottom flask and the selenium dioxide introduced all at once. The flask is fitted with an air condenser and heated in an oil-bath at  $140-150^{\circ}$  for 3-4 hours. The cooled solution is filtered and the selenium washed with acetic acid, and the orange yellow filtrate is carefully neutralised with potassium hydroxide. Camphorquinone is precipitated. The crude product (5.2 g.) is crystallised from ligroin ; m.p.  $198^{\circ}$ . Yield, 4.5 g.

(Note.—The recovered selenium should not be thrown away. It should be collected and may be used for nitrogen determinations by the Kjeldahl method.)



**Preparation 72****BENZOPHENONE OXIME AND BECKMANN REARRANGEMENT**

Benzophenone	... 5 g.
Hydroxylamine HCl	... 3 g.
Rectified spirits	... 50 c.c.
Sodium hydroxide	... 76 g.

A mixture of 5 g. benzophenone, 3 g. hydroxylamine hydrochloride, 10 c.c. water and 50 c.c. rectified spirits is placed in a 250 c.c. round-bottom flask. 6 g. of sodium hydroxide pellets are then added in portions with shaking to the mixture in the flask. When the reaction becomes too vigorous the flask is cooled with tap water. When all the sodium hydroxide has been added, the flask is fitted with a reflux condenser and heated on a boiling water bath for about 5 minutes. The flask is then cooled, the contents poured into 100 c.c. of water containing 3 c.c. of Conc.HCl. The precipitate is filtered at the pump, washed with water and dried in a vacuum desiccator over sulphuric acid. Yield 5 g., m.p. 142°.

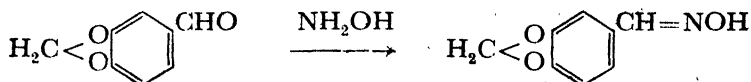
A solution 2 g. of benzophenone oxime in 20 c.c. of anhydrous ether is treated with 3 c.c. of pure thionyl chloride. The solvent is then distilled off and the residue treated with 25 c.c. water. The mixture is boiled for a few minutes, any lumps formed being broken up with a glass rod. The supernatant liquid is decanted off and the residue recrystallised from boiling alcohol. Pure benzanilide so obtained melts at 163°.

**Preparation 73****PIPERONYLAMINE****(a) Piperonal oxime**

Piperonal	... 10 g. (in 15 c.c. alcohol)
Hydroxylamine hydrochloride	... 5 g.
Caustic soda	... 2.5 g. (in 2 c.c. water)

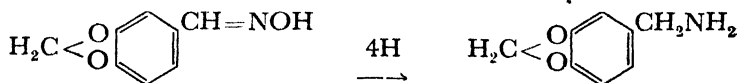
10 g. of piperonal are dissolved in about 15 c.c. of alcohol and 5 g. of hydroxylamine hydrochloride dissolved in the minimum amount of water added. A solution of 2.5 g. of caustic soda in 2 c.c. of water and sufficient alcohol to make

the solution clear are now added and the solution refluxed for three hours on the water-bath. The mixture is poured into 100 c.c. of water and crystals of the oxime that separate are filtered off and recrystallised from boiling water. It is obtained in shining thin prisms; m.p.  $110^{\circ}$ . Yield, 10 g.



(b) **Piperonylamine**

10 g. of piperonal-oxime are dissolved in 40-50 c.c. of alcohol and treated with 125 g. of 5% sodium amalgam at  $50-70^{\circ}$ . The solution is kept acidic by the gradual addition of 50 per cent acetic acid. The alcohol is then distilled off, the residue diluted with water and filtered. The filtrate is cooled and made alkaline with solid potassium hydroxide. The oil is extracted with ether, the ether extract dried over potassium carbonate and the ether then distilled off. The oil is distilled in vacuum, and collects as a thick, colourless liquid boiling at  $136^{\circ}$  to  $138^{\circ}/10$  mm. Yield, 7.5 g.



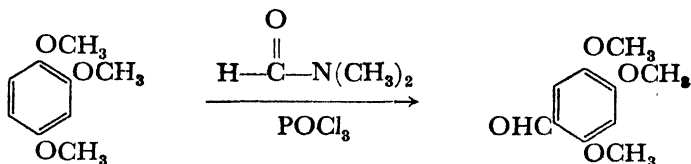
### Preparation 74

2 : 4 : 5-TRIMETHOXYBENZALDEHYDE (ASARYLALDEHYDE)

1 : 2 : 4 Trimethoxy benzene	... 15 g.
Dimethyl formamide	... 10.5 g.
Phosphorous oxychloride (freshly distilled)	... 15 c.c.

A mixture of 15 g. of the trimethoxy benzene, 10.5 g. of dimethyl formamide and 15 c.c. of freshly distilled phosphorous oxychloride is taken in a 250 c.c. round bottom flask fitted with a Liebig condenser and heated on a boiling water bath for 6 hours. 50 c.c. of a saturated solution of sodium acetate in water were then added through the condenser slowly and the contents of the flask refluxed for 30 minutes. On cooling, the aldehyde separates out

in the form of fibrous needles. It is filtered, washed with water and recrystallised from 600 c.c. of boiling water. It crystallises in colourless, slender needles, m.p. 113-114°. Yield, 10.5 g.

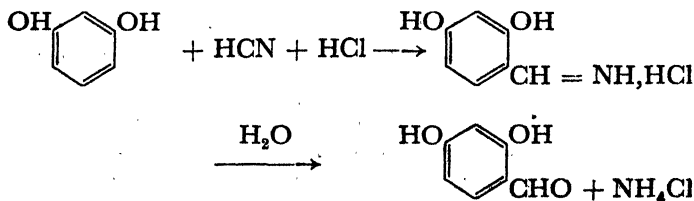


### Preparation 75

#### $\beta$ -RESORCYLIC ALDEHYDE

Resorcinol	... 10 g.
Ether (sodium dried)	... 150 c.c.
Zinc cyanide (anhydrous)	... 14 g.

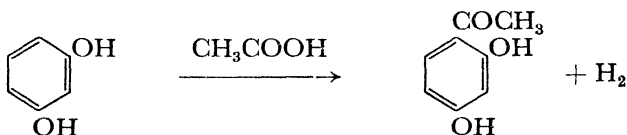
A 500 c.c. bolt-head flask is fitted with a two-holed bung carrying a gas inlet tube and a reflux condenser with a calcium chloride tube attached at the top. Resorcinol, ether (100 c.c.) and the zinc cyanide are introduced into the flask and the solution is saturated with dry hydrogen chloride while the flask is being cooled in ice. The zinc cyanide gradually disappears and the aldimine hydrochloride separates as a thick oil, which solidifies in about 45 minutes. A slow stream of hydrogen chloride is passed continuously at room temperature for a further period of about 4 hours, at the end of which, the ether is decanted and the solid washed twice with dry ether. The aldimine hydrochloride is decomposed by heating under reflux with 20 c.c. of water for 5 minutes on a water-bath. The solution is cooled and left overnight. The crystals that separate are filtered, washed with small amounts of water and dried; m.p. 135°. Yield, 9 g.



**Preparation 76****RESACETOPHENONE**

Zinc chloride (anhydrous)	... 15 g.
Glacial acetic acid	... 15 g.
Resorcinol	... 10 g.

The zinc chloride is fused in a porcelain basin until it shows a tendency to fume, then poured into a clean dry mortar, powdered quickly and kept in a desiccator, ready for use. Glacial acetic acid (frozen and remelted) is taken in a 100 c.c. beaker and the zinc chloride dissolved in it by heating, after which the resorcinol is added. The mixture is heated just to boiling ( $142^{\circ}$ ) and cooled. The syrupy liquid is then treated with a mixture of 40 c.c. of concentrated hydrochloric acid and 40 c.c. of water. Very soon a crystalline mass is obtained which is filtered off and recrystallised from boiling water (100 c.c.). Pale orange yellow plates are obtained, m.p.  $143^{\circ}$ . Yield, 9 g.



*N.B.*—A pure white crystalline product can be obtained by crystallising twice from hot water using norit. The yield however is reduced.

**Alternative method** (Hoesch reaction)

Acetonitrile	... 6 g.
Resorcinol	... 10 g.
Zinc chloride (anhydrous)	... 4 g.

The resorcinol and acetonitrile are dissolved in 25 c.c. of dry ether contained in a 100 c.c. flask and powdered zinc chloride is then added. Dry hydrogen chloride is passed through the mixture for one hour. The zinc chloride gradually dissolves and the mixture which is slightly warm at the beginning becomes cold towards the end and viscous. The flask is corked and left overnight. 25 c.c. of water are added and the clear solution extracted with ether. The aqueous layer is separated and heated for half an hour on a water-bath. On cooling, an oil separates which gradually solidifies on rubbing. This is filtered and recrystallised from

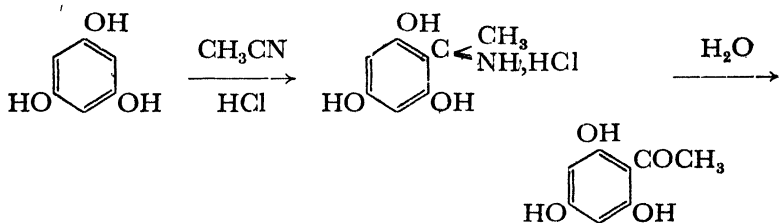
boiling water containing a little hydrochloric acid ; m.p. 144°. Yield, 8 g.

### Preparation 77

#### PHLOROACETOPHENONE

Phloroglucinol	... 20 g.
Acetonitrile (distilled over $P_2O_5$ )	... 13 g.
Ether (anhydrous)	... 80 c.c.
Zinc chloride (freshly fused and powdered)	... 4 g.

A wide-mouthed 250 c.c. bolt-head flask is fitted with a two-holed rubber stopper carrying a gas delivery tube having a wider bore at the delivery end, and a calcium chloride guard-tube. The materials are introduced in the flask in the order indicated above and the flask is well cooled in a freezing mixture of ice and salt. A rapid stream of dry hydrogen chloride is passed through the solution for about 2 hours with occasional shaking. The flask is kept in a refrigerator for 24 hours after which hydrogen chloride is passed for another two hours, cooling in ice as before. The flask is stoppered and left in the refrigerator for three days. A bulky orange yellow precipitate of the ketimine hydrochloride is formed. The ether is decanted and the solid washed twice with 25 c.c. of anhydrous ether. The solid is transferred, by using a litre of hot water in lots, to a two litre flask fitted with an efficient water cooled condenser. The solution is boiled vigorously over a free flame for two hours. The contents are cooled slightly, 5 grams of norit are added and the solution boiled for about five minutes and filtered rapidly through a pre-heated Büchner funnel—the norit is twice extracted with 100 c.c. of boiling water and the combined filtrates allowed to cool overnight. The pale yellow needles of phloroacetophenone are filtered at the pump and dried at 120° in an air oven ; m.p. 218-219°. Yield, 22 g.



**Preparation 78****QUINOACETOPHENONE**

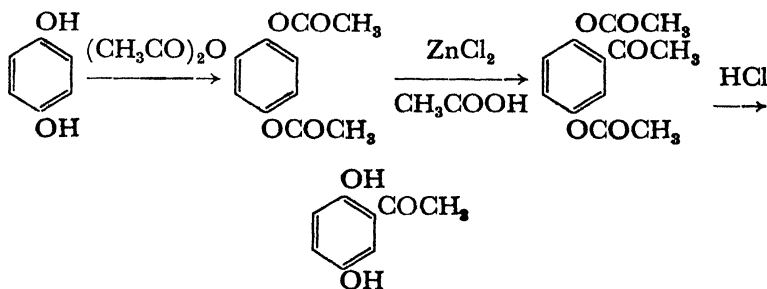
Hydroquinone	... 10 g.
Acetic anhydride (freshly distilled)	... 12 g.
Sodium acetate (freshly fused)	... 10 g.
Glacial acetic acid (frozen and melted)...	10 c.c.
Zinc chloride (fused and powdered)	... 10 g.
Hydrochloric acid (1 : 1)	... 100 c.c.
Sodium hydroxide (10% solution)	... 100 c.c.

**(a) Hydroquinone diacetate**

The hydroquinone, acetic anhydride and the sodium acetate are introduced into a 100 c.c. round bottom flask fitted with a Liebig condenser and the mixture refluxed for two hours. The melt is then poured over crushed ice in a 250 c.c. beaker. The solid that separates is filtered and crystallised from alcohol using norit ; m.p. 211-122°. Yield, 14 g.

**(b) Quinoacetophenone**

The fused zinc chloride is dissolved in the glacial acetic acid contained in a 500 c.c. bolt-head flask and the quinol diacetate added. The mixture is boiled gently under reflux for about 9 hours, guarding from moisture by using a calcium chloride guard-tube. It is then cooled, and treated with the (1 : 1) hydrochloric acid and left overnight. The solid that separates is filtered and dissolved in a solution of sodium hydroxide and filtered to remove any unhydrolysed diacetate. The filtrate is acidified with hydrochloric acid. The precipitated solid is filtered, washed with water and then crystallised from dilute alcohol ; m.p. 202°. Yield, 5 g.

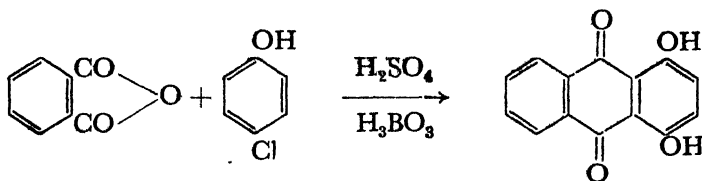


**Preparation 79**

## QUINIZARIN

<i>p</i> -Chlorophenol	... 16.5 g.
Phthalic anhydride	... 43 g.
Boric acid	... 7 g.
Conc. sulphuric acid	... 286 g. (152 c.c.)

The above compounds are mixed thoroughly in a round-bottom flask of one litre capacity and gradually heated in an oil-bath to 200°, at which it is maintained steadily for about three and a half hours. Owing to the tendency of phthalic anhydride to sublime, the mouth of the flask is closed by a porous plate. When quite cold, the contents of the flask are poured into about 720 c.c. of cold water with constant stirring and filtered. The precipitate is boiled with 1½ litres of water and filtered hot to remove the excess of phthalic anhydride which dissolves. The residue is suspended in 1½ litres of boiling water in a 2 litre round-bottom flask and treated with a sufficient amount (about 5 c.c.) of 10N potassium hydroxide solution to produce a purple colour, followed by 40 c.c. more. The alkaline solution is filtered hot and the residue washed with 30 c.c. of hot 2% potassium hydroxide solution, the residue being discarded. The purple quinizarin solution is saturated with carbon dioxide and the precipitated quinizarin again filtered. The product is then boiled with 720 c.c. of a 10% sodium carbonate solution until it appears black so as to dissolve the last traces of purpurin. The mixture is cooled to room temperature, filtered and the precipitate boiled with 720 c.c. of 5% hydrochloric acid to liberate the quinizarin. On cooling, the quinizarin is precipitated. The product is filtered, washed with water and dried at 100°; m.p. 195°. Yield, 18 g.





**Preparation 80****BENZOYLACETONE**

Ethyl acetate (pure)	... 13 g.
Acetophenone	... 15 g.
Anhydrous ether	... 200 c.c.
Sodamide	... 10 g.

The ethyl acetate and acetophenone are dissolved in 100 c.c. of anhydrous ether contained in a 500 c.c. round-bottom flask fitted with a reflux condenser. 10 g. of finely powdered sodamide are added a little at a time. The reaction is very vigorous, plenty of ammonia is evolved and the flask is cooled in ice water, if necessary, to moderate the reaction. The flask should be shaken after each addition. The sodium salt of the diketone separates as a yellow mass and the flask is set aside for 24 hours after adding another 50 c.c. of ether through the condenser. The sodium salt is then poured into ice water sufficient to dissolve it completely. The aqueous layer is separated from the ether layer, and air is aspirated through the aqueous layer to remove the dissolved ether. The solution is filtered and glacial acetic acid is added till the solution is acid. Benzoylacetone is precipitated as a cream coloured solid which is filtered and washed with water. It is air-dried for a day and crystallised from ligroin. Colourless crystals; m.p.  $61^{\circ}$ . Yield, 13 g.

**Preparation 81****BENZYLACETONE****(a) Benzyl acetoacetic ester**

Sodium	... 3 g.
Absolute alcohol	... 38 c.c.
Acetoacetic ester	... 32.5 g.
Benzyl chloride	... 16 g.

The alcohol is introduced into a 250 c.c. round-bottom flask fitted with a reflux condenser and the sodium added in bits. The freshly distilled acetoacetic ester is added after all the sodium has dissolved. The benzyl chloride is added later and the mixture kept at room temperature for an hour after which it is refluxed for another hour. The condensation product is

distilled under reduced pressure (14 mm.) collecting the distillate at 164-165°. The unreacted acetoacetic ester passes over below 160°. Colourless oil, b.p. 165°/14 mm. ; 290°/760 mm. Yield, 23 g.

(b) **Benzylacetone** (Ketonic hydrolysis)

Benzyl acetoacetic ester ... 16 g.

Caustic potash (in 90 c.c. water) ... 9 g.

The ester is boiled under reflux in a 250 c.c. round-bottom flask with the caustic potash solution for five hours. At the end of this period the reaction is complete and the contents of the flask are distilled. A colourless oil passes over along with water. The oil is extracted with ether. The ethereal solution is dried over calcium chloride, and after removal of ether by distillation, the residual oil is distilled under atmospheric pressure or reduced pressure when the ketone passes over as a light colourless oil, b.p. 236°/760 mm. Yield, 8 g.

## Preparation 82

### BENZYLACETOPHENONE

(a) **Acetophenone**

Benzene (dry) ... 15 g.

Aluminium chloride anhydrous ... 25 g.

Acetyl chloride (redistilled) ... 18 g.

The re-sublimed aluminium chloride is introduced into a 250 c.c. round-bottom flask and immediately covered with dry benzene. The flask is fitted with a reflux condenser, surrounded by ice water and acetyl chloride is added through the top of the condenser from a dropping funnel. A vigorous evolution of hydrogen chloride takes place. After allowing the mixture to stand for an hour, the brown viscid mass is poured into a one litre beaker containing a mixture of ice and water (200 c.c.). The mass decomposes with evolution of heat and the dark oil separating is extracted with benzene in a separating funnel. The benzene solution is washed once with caustic soda, then with water, and finally dried over calcium chloride. The benzene is first distilled off using a water condenser, and then the acetophenone using an air condenser, the distillate being collected between 195-205°. It is obtained

as a colourless liquid with a pleasant odour; m.p.  $20.5^{\circ}$ , b.p.  $202^{\circ}$ . Yield, 11 g.

### Alternative method

Acetyl chloride	... 10 g.
Dry benzene	... 10 g.
Mercuric chloride	... 10 g.
Aluminium powder	... 0.5 g.

The dry benzene and mercuric chloride are introduced into a bolt-head flask of 250 c.c. capacity fitted with a reflux condenser and the aluminium powder is added gradually with vigorous shaking. If the reaction becomes violent it is moderated by immersing the flask in ice water. A green crystalline mass separates and the reaction is completed by warming on a water-bath for half an hour. The mercury liberated in the reaction is removed and the acetyl chloride is added through the condenser in small quantities, the reaction mixture being agitated by a mechanical stirrer. After standing for two hours the flask is heated to  $40^{\circ}$  for an hour. After cooling, water is added to decompose the product and the liberated oil extracted with benzene. The extract is dried over calcium chloride and fractionated, the fraction distilling between  $195-205^{\circ}$  being collected. Yield, 9 g.

### (b) Benzalacetophenone

Acetophenone	... 10 g.
Benzaldehyde	... 9 g.
Sodium hydroxide	... 4 g. (in 38 c.c. water)
Alcohol	... 13 c.c.

The sodium hydroxide is dissolved in water at first and added to the alcohol contained in a 300 c.c. wide-mouthed bolt-head flask covered with a perforated disc for the passage of a stirrer. The flask is cooled in ice and the acetophenone added. The mixture is stirred vigorously and the benzaldehyde (freshly distilled) is added all at once. The temperature is kept between  $15-25^{\circ}$ . After two hours stirring, the mixture becomes thick and is left over-night in the refrigerator. The mixture is centrifuged, washed with water till the washings are neutral to litmus, filtered and finally washed with cold alcohol (10-15 c.c.). It is purified by recrystallisation from 4 to 5 times its weight of alcohol. A solution may be used for this purpose; m.p.  $62^{\circ}$ . Yield, 14 g.

**(c) Benzylacetophenone**

This is obtained by reduction of benzalacetophenone with hydrogen in the presence of platinum oxide catalyst.

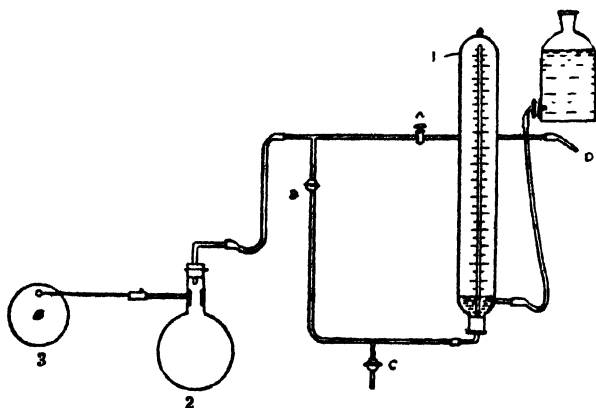


Fig. 43. Apparatus for reduction with platinum oxide catalyst. 1. Reservoir of hydrogen. 2. Bolt-head flask containing substance in solution. 3. Eccentric shaking device.

**Reduction.** 10.4 g. of benzalacetophenone are dissolved in 75 c.c. of pure dry ethyl acetate in a bolt-head flask of 300 c.c. capacity fitted with a tight fitting one-holed rubber stopper, carrying a glass tube with a right-angled bend. 0.2 g. of the platinum oxide catalyst is added, the air in the flask is displaced by hydrogen which has been purified by passing through two wash bottles containing mercuric chloride and potassium permanganate respectively. The flask is then connected to the reservoir of hydrogen and mechanically shaken (Fig. 42). The hydrogen to be absorbed is about .05 mole (1.12 litres at N.T.P.). When the reaction is over (1-1.5 hours), the platinum is filtered off and the solvent removed by distillation under reduced pressure. The benzylacetophenone is recrystallised from 10 c.c. of alcohol; m.p. 73°. Yield, 7 to 8 g.

**Manipulation.** By keeping stop-cocks A and B closed and C open, the aspirator bottle is raised so that the reservoir is full of water and the tap C then closed. The aspirator is lowered and the hydrogen Kipp connected at D and the taps A and B opened. Hydrogen collects in the reservoir displacing the water

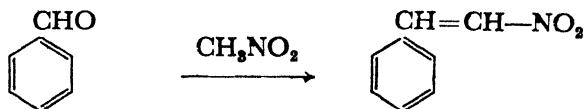
into the aspirator. When the reservoir is full of gas, tap A is closed and B kept open. Tap C is used to remove any water collecting in the bends.

### Preparation 83

#### $\omega$ -NITROSTYRENE

Benzaldehyde (freshly distilled)	... 13 g.
Nitromethane	... 8 g.
Methanol	... 50 c.c.
Sodium hydroxide	... 5.3 g. (in 13 c.c. of water.)

The benzaldehyde and nitromethane are dissolved in 50 c.c. of methyl alcohol contained in a wide-mouthed bolt-head flask cooled in a freezing mixture of ice and salt. The mixture is stirred mechanically and the sodium hydroxide solution added from a dropping funnel at such a rate that the temperature does not rise above 10-15°. The first few c.c. must be added very carefully as there is a period of induction for the reaction and unless care is taken, the temperature may suddenly shoot up. As the condensation proceeds, a bulky white precipitate is obtained and more methyl alcohol is added if the mixture thickens. The reaction is taken as complete when a test portion dissolves completely in water. To the reaction mixture 75 c.c. of ice water are added and the solution run into cooled dilute hydrochloric acid (25 c.c. of concentrated hydrochloric acid in 38 c.c. of water) little by little with vigorous stirring. The crude nitrostyrene separates as a yellow crystalline mass which is filtered and washed with water. It is purified by crystallisation from alcohol; m.p. 57-58°. Yield, 14 g.

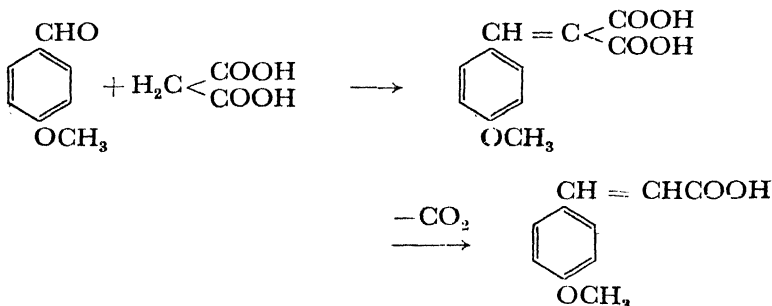


*Note.*—The reverse process of adding the acid to the reaction mixture should never be attempted as the product obtained is an oil containing a saturated nitro alcohol.

**Preparation 84*****p*-METHOXYCINNAMIC ACID**  
(Knoevenagel reaction)

Anisaldehyde (freshly distilled)	... 13.6 g.
Malonic acid	... 12.6 g.
Ammonia (8%) in ethyl alcohol	... 21 g.

The anisaldehyde and malonic acid are dissolved in the minimum amount of absolute alcohol in a 250 c.c. conical flask and the alcoholic ammonia added to the solution. The flask is corked and left to stand for 10-15 minutes. The alcohol is then distilled off on a water-bath and the oily residue in the flask heated on a vigorously boiling water-bath till the evolution of carbon dioxide ceases and the mixture becomes solid (2 hours). The residue is then dissolved in the minimum amount of sodium carbonate solution and the resulting liquid boiled with 1-2 g. of norit and filtered. The warm filtrate is poured into an excess of 20% sulphuric acid containing crushed ice. The precipitated acid is filtered, washed with water and dried. Yield 8 g. It is recrystallized from boiling water or alcohol. M.P. 172°.

**Preparation 85****COUMARIN****(a) Salicylaldehyde**

Phenol	... 40 g.
Chloroform	... 60 g.
Caustic soda (in 100 c.c. of water)	... 80 g.

The caustic soda solution is introduced into a litre round-bottom flask and the melted phenol dissolved in it. The flask is fitted with a reflux condenser. The chloroform is added through the condenser in lots of 5 c.c. and the flask is well shaken after each addition. Throughout the addition, the temperature is kept at 60-65° by immersion in a hot water-bath. The colour changes from yellow through violet to deep red. The mixture is then refluxed for half an hour and the termination of the reaction is indicated by the separation of a yellow semi-solid mass. The unreacted chloroform is removed by distillation on a water-bath, the residual liquid is diluted with water, carefully neutralised with dilute sulphuric acid and steam distilled till no more oily drops pass over. The distillate consists of a mixture of salicylaldehyde and phenol and these two can be separated only through the formation of the bisulphite compound of the aldehyde. The distillate is extracted with ether and the ethereal solution shaken with a freshly prepared saturated solution of sodium bisulphite continuously till no more crystals of the bisulphite compound are obtained. The crystals are filtered, washed with alcohol to remove traces of phenol and decomposed by heating with dilute sulphuric acid on water bath. The aldehyde is extracted with ether, dried over calcium chloride and after removal of ether distilled. It is obtained as a colourless fragrant oil, b.p. 196.5°. Yield, 8 g.

***p*-Hydroxybenzaldehyde.** The resinous mass left over in the flask after steam distillation is filtered hot and from the brownish aqueous filtrate the para compound is obtained by extraction with ether. The aldehyde separates in fine needle-shaped crystals, m.p. 116°. Yield, 1-2 g.

**(b) Coumarin**

Salicylaldehyde	... 15 g.
Acetic anhydride	... 20 g.
Sodium acetate (freshly fused)	... 25 g.
Iodine	... 0.5 g.

The mixture of the above is taken in a 250 c.c. round-bottom flask fitted with an air condenser and heated at first for 2 hours in an oil-bath at 120° after which the temperature is raised to 180°-190° and the heating continued for another 4 hours. The product is poured into water and extracted with ether. The

ether solution is shaken with a freshly-prepared saturated solution of sodium bisulphite to remove unchanged salicylaldehyde. The ether solution is separated, dried over calcium chloride and the ether distilled off. The residue is distilled under diminished pressure (b.p.  $160^{\circ}$  at 20 mm., or  $210-220^{\circ}$  at 40 mm.). The distillate is extracted with small quantities of boiling ligroin. The combined extract on evaporation furnishes crystals of coumarin, m.p.  $67^{\circ}$ . Yield, 7 g.

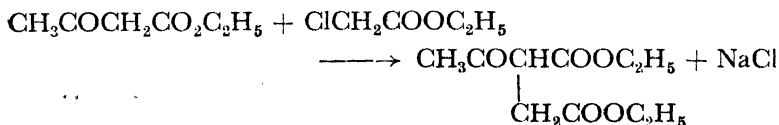
### Preparation 86

#### 3-CARBETHOXYMETHYL-7-HYDROXY-4-METHYLCOUMARIN

##### (a) Ethyl acetosuccinate.

Sodium	... 5.8 g.
Ethyl chloracetate	... 31 g.
Ethyl acetoacetate	... 33 g.
Absolute alcohol	... 70 g.
Benzene	... 70 g.

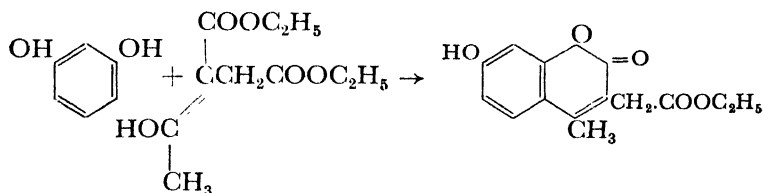
The sodium in the form of clean wire is dissolved in absolute alcohol contained in a 500 c.c. round-bottom flask fitted with a reflux condenser and the solution treated with a freshly distilled acetoacetic ester. The condenser is removed and the flask fitted with a one-holed cork and bent tube and the solution is evaporated to dryness in a vacuum. The solid residue is then broken and mixed with benzene, the chloracetic ester added and the whole boiled under reflux for two hours on a water-bath. The benzene is then distilled off, the residue poured into water and the ester extracted with ether. The ether extract is dried over anhydrous potassium carbonate and after removal of ether, the residual oil is distilled under diminished pressure, the portion boiling at  $135^{\circ}/10$  mm., being collected. B.P.  $256^{\circ}\text{d}/760$  mm. Yield, 33 g





**(b) 3-Carbethoxymethyl-7-Hydroxy-4-Methylcoumarin**

Ethyl acetosuccinate (8 g.) and resorcinol (4 g.) are mixed into a thin cream and slowly added to concentrated sulphuric acid (12 c.c.) cooled in ice, the flask being shaken after each addition. The deep-red liquid is kept in an ice chamber or in a refrigerator overnight and then poured into 100 c.c. of water. The precipitated solid is filtered off after keeping for two hours, washed well with water and then with 50 c.c. of 25% alcohol, dried and recrystallised from boiling alcohol. It crystallises in colourless needles, m.p. 163°. Yield, 6 g.

**Preparation 87**

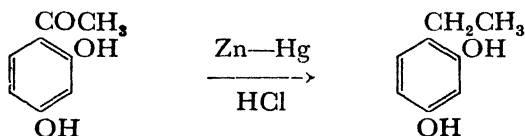
ETHYLRESORCINOL  
(Clemmensen reduction)

Resacetophenone	... 10 g.
Zinc amalgam from	... 40 g. of zinc
Concentrated hydrochloric acid	... 30 c.c.

**Preparation of zinc amalgam.** 40 g. of zinc (either as strips from foil or zinc turnings, small pieces of granulated zinc or mossy zinc) are placed in a 250 c.c. round-bottom flask and washed thrice with warm 1 : 1 hydrochloric acid. 40 c.c. of water, 2 to 4 g. mercuric chloride and 2 c.c. of concentrated hydrochloric acid are added to the washed zinc and vigorously stirred for about ten minutes. The aqueous solution is decanted off, the amalgamated zinc is washed once with distilled water and covered with 30 c.c. water and an equal volume of concentrated hydrochloric acid.

**Reduction of the carbonyl group to methylene group.** 10 g. of resacetophenone are added to the amalgam contained in the

flask and the mixture is refluxed for about 3-4 hours, 5 c.c. of concentrated hydrochloric acid being added every hour. At the end of each hour a drop of the liquid is taken in ethyl alcohol (say 1 c.c.) and tested with aqueous ferric chloride. If no colour is seen, it means the reaction is over. When the reaction is over, the contents of the flask are cooled, and the supernatant liquid carefully decanted from the unreacted amalgam. The solution is then saturated with solid sodium chloride (table salt), cooled and extracted repeatedly with ether. The combined ether extracts are dried over anhydrous sodium sulphate. On removal of the ether, a light yellow solid is obtained. It is crystallised from benzene or chloroform. Ethyl resorcinol crystallises in white glistening prisms, m.p.  $97^{\circ}$ . Yield, 11 g.



### Preparation 88

DIBENZYL FROM BENZIL  
(Clemmensen reduction)

Benzil	...	7 g.
Amalgamated Zinc	...	30 g.
Hydrochloric acid (1 : 1)	...	100 c.c.
Concentrated hydrochloric acid	...	20 c.c.

**Preparation.** The benzil, hydrochloric acid and the amalgamated zinc are introduced into a 250 c.c. round-bottom flask fitted by a ground joint to a long air-condenser and the mixture kept boiling gently for about 4 hours. 5 c.c. of concentrated hydrochloric acid are added at the end of each hour. The clear liquid is decanted into a beaker and the reaction product which solidifies is separated by filtration and washed with water repeatedly. It is recrystallised from alcohol; m.p.  $52^{\circ}$ , b.p.  $280^{\circ}$ . Yield, 5 g.



**Preparation 89****2-ALLYLPHENOL**

(Claisen rearrangement)

**(a) Allyl phenyl ether**

Phenol	... 18.8 g.
Allyl bromide	... 24.2 g.
Potassium carbonate (freshly calcined and finely ground)	... 28 g.
Acetone (dry)	... 30 g.

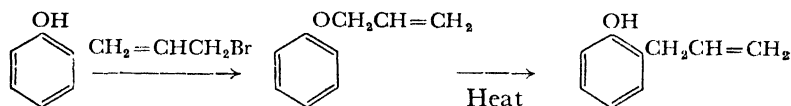
The phenol, allyl bromide, potassium carbonate and acetone are introduced into a 250 c.c. round-bottom flask fitted with a double surface water-cooled condenser and heated on a boiling water bath for about 8 hours. The contents of the flask are then transferred to a 500 c.c. separating funnel and extracted repeatedly with ether after addition of 100 c.c. water. The ether extract is washed twice with 2N sodium hydroxide to remove any unreacted phenol and then with water to free it from alkali and dried over anhydrous potassium carbonate. After removal of ether, the residue, which is allyl phenyl ether, is purified by distillation under reduced pressure; b.p.  $85^{\circ}/19$  mm.  $n_D^{30}$  0.9831, Yield, 22 g.

**(b) 2-Allylphenol** (Claisen rearrangement)

The allyl phenyl ether is heated in a flask fitted with a long air condenser over a sand bath and kept gently refluxing. The progress of the reaction is followed by measuring the refractive index with the Abbe Refractometer at frequent intervals. The time of complete change is about 5-6 hours. When the refractive index has risen to 1.5433 from its initial value of 0.9831, the transformation may be taken as complete. During the rearrangement, a small quantity of 2-methyl-dihydrobenzofuran is formed as a by-product. So, the 2-allylphenol is obtained pure from the reaction as follows :

The distilled product is dissolved in twice its volume of 20% sodium hydroxide solution and the alkaline solution is extracted twice with 30 c.c. of petroleum ether to remove the dihydro benzofuran. The alkaline solution is then acidified with dilute hydrochloric acid and extracted repeatedly with ether. The

ether extract is dried over anhydrous calcium chloride. After removal of ether the 2-allylphenol is distilled under reduced pressure ; b.p. 103-105.5°/19 mm. 220°/760 mm.  $n_D^{30}$  1.5453 ; yield, 15 g.



### Preparation 90

#### 2-HYDROXY-5-METHYLBENZOPHENONE (Fries rearrangement)

<i>p</i> -Cresol	... 10 g.
Benzoyl chloride	... 10 c.c.
Sodium hydroxide (2N)	... 20 c.c.
Aluminium chloride (anhydrous, resublimed)	... 8 g.
Concentrated hydrochloric acid	... 20 c.c.

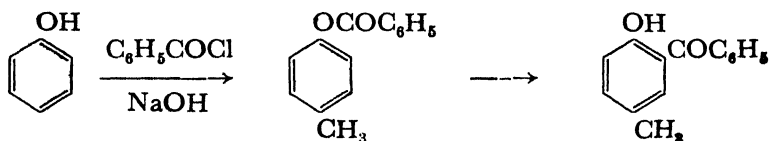
##### (a) *p*-Cresyl benzoate

10 g. of *p*-cresol are taken in a 300 c.c. round bottom flask and 100 c.c. of water followed by 10 c.c. of benzoyl chloride are then added. To this mixture enough sodium hydroxide solution (2N) is added till strongly alkaline and the flask shaken vigorously after suitably corking it. Heat is evolved and the flask is cooled under the tap. After shaking intermittently for about half an hour, the contents are tested for alkalinity. If the liquid is not alkaline more alkali is added and the process repeated. The oily product is poured into ice water and rubbed with a glass rod to induce crystallisation. The solid is filtered, washed with plenty of water and crystallised from 50% alcohol. The crystals are filtered at the pump and dried in a vacuum desiccator over concentrated sulphuric acid. Yield, 12 g. m.p. 71°.

##### (b) 2-Hydroxy-5-methylbenzophenone

*p*-Cresyl benzoate (10 g.) and anhydrous aluminium chloride (8 g.) are introduced into a 250 c.c. bolt-head flask fitted with a

two-holed cork carrying a thermometer and an air condenser. A calcium chloride guard-tube is attached to the air condenser. The reactants are mixed by shaking the flask and the flask is then heated in an oil-bath kept at  $90^{\circ}$ . After the reaction mixture has completely melted the temperature of the bath is raised rapidly to  $120^{\circ}$  and then slowly to  $140^{\circ}$  at which it is kept for about 10-15 minutes. Heating is then stopped; the thermometer is removed and when the flask is cold, the contents are poured into 50 g. of ice and 20 c.c. of concentrated hydrochloric acid. When the ice has melted, the product is filtered. The hydroxy benzo-phenone is recovered from the precipitate by distillation in superheated steam. It is further purified by crystallisation from alcohol, m.p.  $83-84^{\circ}$ . Yield, 8 g.



### Preparation 91

#### $\alpha$ -NAPHTHYLACETIC ACID (Arndt-Eistert Reaction)

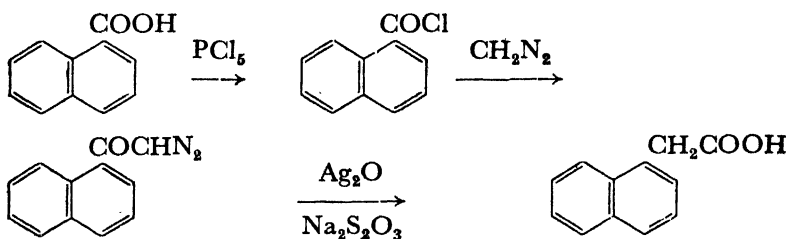
$\alpha$ -Naphthoic acid	... 10 g.
Nitrosomethyl urea	... 18 g.

**Preparation of diazomethane solution.** A mixture of 200 c.c. of ether and 55 c.c. of 40% aqueous potassium hydroxide is cooled to  $5^{\circ}$ . To this is added with continuous cooling and efficient stirring 18 g. of nitrosomethyl urea in small portions as rapidly as the crystals dissolve. The deep yellow ethereal solution of diazomethane is separated by means of a separating funnel and dried over pure potassium hydroxide pellets for an hour. The solution contains about 5 g. of diazomethane. (*Diazomethane is exceedingly toxic and great care must be taken in handling and inhalation of its vapours must be avoided. The experiment should be conducted in an efficient fume cupboard.*)

**Preparation of  $\alpha$ -Naphthoyl chloride.** A mixture of 10 g. of  $\alpha$ -Naphthoic acid and 12 g. of phosphorous pentachloride is placed in a 100 c.c. distilling flask and heated on a water-bath (hood) until no more hydrogen chloride is evolved. The phosphorous oxychloride is then removed by distillation under reduced pressure (water pump). The residue is then distilled using an oil pump. The  $\alpha$ -Naphthoyl chloride is collected at  $168^\circ/10$  mm. Yield, 9.5 g.

**$\alpha$ -Naphthylacetic acid.** A solution of 9.5 g. of  $\alpha$ -Naphthoyl chloride in 25 c.c. of dry ether is added dropwise to an ethereal solution of diazomethane, prepared from 18 g. of nitroso-methyl urea at  $10^\circ$ . After keeping at  $20-25^\circ$  for six hours, the ether is removed *in vacuo* at  $30^\circ$  (water pump). The residue (9 g.) is  $\alpha$ -naphthyl diazoketone. A small portion is crystallised from a little benzene. It melts at  $54-55^\circ$ .

A solution of 3 g. of the diazoketone in 25 c.c. of dioxane is added to a solution of 2 g. silver oxide and 3 g. sodium thiosulphate in 100 c.c. water at  $50-60^\circ$  with stirring. The stirring is continued till nitrogen evolution ceases (1 hour). The solution is then cooled, made acidic with dilute nitric acid and the precipitated acid crystallised from water using norit; m.p.  $130^\circ$ , yield, 1.4 g.



## Preparation 92

### TRIPHENYL CARBINOL.

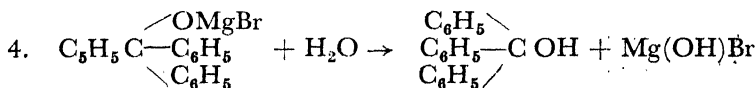
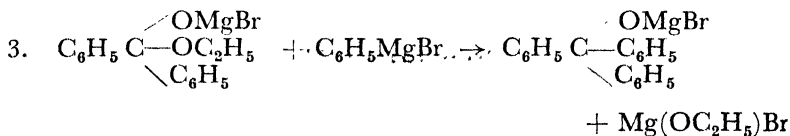
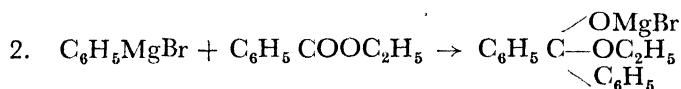
(Grignard reaction)

Bromobenzene	...	27 g.
Magnesium	...	3.2 g.

Methyl benzoate	... 21 g.
or	
Ethyl benzoate	... 24 g.
Ether (dry)	... 100 c.c.

The preparation of this substance involves the preparation of a Grignard reagent as a preliminary step. All the materials used for preparing the Grignard reagent should be scrupulously freed from impurities and dried.

**Preparation of the Grignard reagent.** 3.2 g. of clean magnesium turnings or ribbon in small pieces are washed with ether, dried at 110-120° in an air-oven and introduced into a dry round-bottom flask of 300 c.c. capacity, fitted with a one-holed cork carrying an upright dry condenser protected by a calcium chloride tube and containing pure dry bromobenzene (27 g.) dissolved in about 70 c.c. of ether. A fragment of iodine is added if necessary to start the reaction and the flask warmed on a water-bath until the magnesium has completely dissolved. Freshly distilled methyl benzoate (21 g.) or ethyl benzoate (24 g.) dissolved in 40 c.c. of ether is added to the cold solution slowly with constant shaking. The mixture is boiled under reflux for an hour, cooled and acidified with dilute hydrochloric acid till just acid after adding crushed ice. The ether is removed by distillation and the residue steam distilled to remove unacted bromobenzene as well as any diphenyl formed. The triphenyl carbinol which remains over is filtered, dried and crystallised from benzene. Colourless needles, m.p. 162.5°. Yield, 11 g.

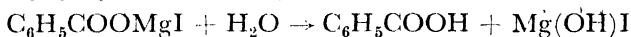
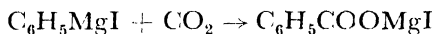
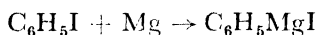


**Preparation 93****BENZOIC ACID**

(Grignard reaction).

Magnesium	... 2.6 g.
Dry ether	... 40 c.c.
Iodobenzene	... 20.4 g.

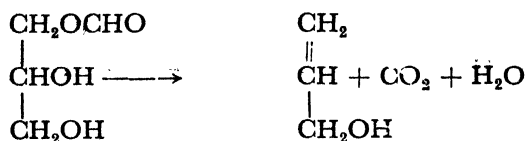
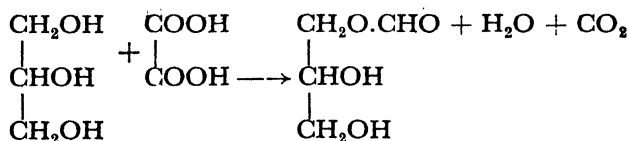
The mixture of magnesium, ether and iodobenzene with a fragment of iodine is taken in a flask of 250 c.c. capacity and the preparation of the Grignard reagent carried out as detailed previously. A white flocculent precipitate is seen to form and when all the magnesium has dissolved (about 2 hours) the flask is cooled in ice water, the condenser is removed and a slow current of carbon dioxide washed first by sodium carbonate solution (1 wash bottle), and dried by concentrated sulphuric acid (2 wash bottles) is led into the ethereal solution. Cooling should be continued throughout. The reaction mixture separates into two layers, an upper layer of ether and a heavy lower layer of the reaction product. Powdered ice is added and then slowly 30 c.c. of (1 : 1) hydrochloric acid. The precipitated benzoic acid is extracted by the ether. After removal of the ether by distillation, the crude acid obtained is dissolved in dilute alkali, the solution filtered and the acid reprecipitated by dilute hydrochloric acid; m.p. 121°. Yield, 10 g.

**Preparation 94*****L*-ALLYL-*L*-PHENYLBENZYL ALCOHOL****(a) Allyl Alcohol**

Oxalic acid	... 25 g.
Glycerol	... 100 g.
Ammonium chloride	... 0.25 g.



The mixture in quantities indicated above is introduced into a 250 c.c., distilling flask, fitted with a one-holed cork carrying a thermometer, which is so adjusted that the bulb is fully immersed in the liquid without touching the bottom of the flask. A long air condenser is attached to the side-tube, the flask is heated on a sand bath or over a wire gauze using a rose top for the burner, and the distillate is caught in a receiver. A rapid evolution of carbon dioxide is noticed which stops after a time when the temperature reaches about 180°. Formic acid collects up to a temperature of 195°. When the temperature reaches 200° the receiver is changed, and a further decomposition with a brisk evolution of carbon dioxide takes place. The distillation is continued till a temperature of 250° is reached. An oily distillate, which is a mixture of allyl alcohol, water, allyl formate and acrolein, having a disagreeable odour, collects. This is redistilled over a free flame till about 80% of the liquid has collected. The liquid is saturated with solid potassium carbonate and the oily layer of allyl alcohol separated and purified by distillation, the part coming over between 93-97° being collected. It is a colourless liquid with a pungent odour, miscible with water, b.p. 96.6°, sp. gr. 0.871. Yield, 9 g.



**(b) Allyl bromide**

Hydrobromic acid (48%)	... 100 g.
Concentrated sulphuric acid	... 30 g.
Allyl alcohol (aqueous) containing	
24 g. pure alcohol)	... 38.5 c.c.

The apparatus (Fig. 41) is set up with the condenser set for downward distillation, the capacity of the flask being 500 c.c.

A mixture of concentrated sulphuric acid and hydrobromic acid is first introduced into the flask and the aqueous allyl alcohol then added. The stirring is started and another 30 g. of concentrated sulphuric acid are gradually added from the tap funnel, to the warm solution. The allyl bromide distils over in about an hour. The crude bromide is washed with dilute sodium carbonate solution, dried over anhydrous calcium chloride and redistilled. B.P. 69-72°. Yield, 45 g.

(c) **1-Allyl-1-phenyl benzyl alcohol**

Magnesium turnings	... 4 g.
Allyl bromide	... 20 g.
Acetophenone	... 20 g.

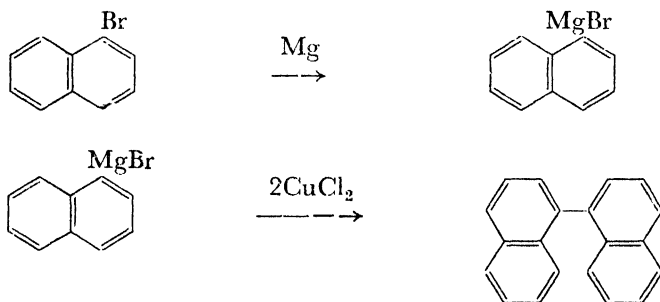
The magnesium turnings, 1 c.c. of allyl bromide and 15 c.c. of dry ether are taken in a dry 500 c.c. round bottom flask fitted with a reflux condenser carrying a calcium chloride tube at the top. On adding two small iodine crystals a vigorous reaction sets in and when it shows signs of slackening, a mixture of the ketone and the allyl bromide dissolved in an equal amount of dry ether is added gradually from a dropping funnel in drops. The reaction becomes very vigorous and is moderated if necessary, by surrounding the flask with cold water and adding a little ether. When all the solution has been added, the reaction mixture is heated under reflux for half an hour. The mixture is poured carefully into cooled aqueous ether and decomposed eventually by adding ice and dilute sulphuric acid. The ether extract is washed with water, dried over potassium carbonate and fractionally distilled under reduced pressure after removal of ether. The crude product obtained in the first distillation is redistilled and the pure alcohol distilling over at 104-105°/24 mm. is collected. B.P. 218-220°/760 mm. Yield, 18 g.

## Preparation 95

### 1 : 1' -BINAPHTHYL

1-Bromonaphthalene	... 20.7 g.
Magnesium turnings	... 2.4 g.
Cupric chloride	... 13.5 g.

A mixture of 2.4 g of magnesium turnings, 20 c.c. dry ether and 20.7 g. of  $\alpha$ -bromonaphthalene and a small crystal of iodine is warmed gently until the reaction is initiated. A precipitate forms in the reaction mixture and 25 c.c. of sodium-dried benzene is added to dissolve the precipitate. The mixture is then heated on a water-bath till all the magnesium is consumed. The preparation is carried out in a round-bottom flask fitted with an efficient reflux condenser (calcium chloride guard tube). The solution of  $\alpha$ -naphthylmagnesium bromide is then poured with good cooling and stirring into a suspension of 13.5 g. of anhydrous cupric chloride in 50 c.c. ether. Moisture is to be excluded during this operation. The reaction mixture is heated under reflux for one hour and then treated with water and dilute hydrochloric acid until the cupric chloride is in solution. The organic layer is separated, washed successively with dilute hydrochloric acid, dilute ammonia solution and water and dried over calcium chloride. After removal of the solvent, 1:1'-binaphthyl m.p.  $154^\circ$  is obtained. Yield, 10 g.



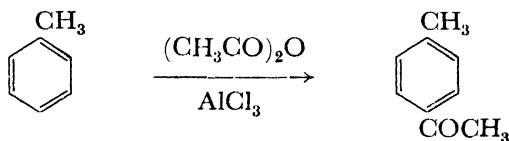
### Preparation 96

*p*-METHYLACETOPHENONE  
(Friedel-Crafts reaction)

Toluene	... 65 c.c.
Aluminium chloride (anhydrous)	... 38 g.
Acetic anhydride (freshly distilled)	... 12 c.c.

In a 500 c.c. three-necked flask provided with a separating funnel carrying a calcium chloride guard tube, a mercury-sealed

mechanical stirrer and a double surface reflux condenser attached to a gas absorption device, 38 g. of freshly sublimed aluminium chloride and 65 c.c. of sulphur-free sodium-dried toluene are placed. The stirrer is set in motion and 12 c.c. of freshly distilled acetic anhydride are added through the separating funnel during about twenty minutes. The temperature rises to about  $90^{\circ}$  and much hydrogen chloride is evolved. The mixture is then heated on a water bath for about 30 minutes till the gas evolution ceases, cooled to room temperature and poured into a mixture of 100 g. crushed ice and 100 c.c. of concentrated hydrochloric acid. After stirring to effect dissolution of the aluminium salts, the toluene layer is separated, washed successively with water, 10% sodium hydroxide solution till the washings are alkaline and finally with water. After drying over anhydrous sodium sulphate, the liquid is distilled at atmospheric pressure till the temperature rises to  $125^{\circ}$  and then cooled and distilled under reduced pressure. The *p*-methylacetophenone distils over at  $93-94^{\circ}/7$  mm. (the b.p. under atmospheric pressure is  $225^{\circ}$ ). Yield, 14 g.



## Preparation 97

### ACETOPIPERONE

#### (a) Piperonylic acid

Piperonal	... 35 g.
Potassium permanganate	... 53 g.
Sodium hydroxide solution (10%)	... 300 c.c.

In a 3-litre round-bottom bolt-head flask 35 g. of piperonal and 800 c.c. of water are introduced and heated to  $70-80^{\circ}$  on a boiling water-bath with mechanical stirring. As the emulsion is being stirred, a solution of 53 g. potassium permanganate in one litre of water is allowed to flow into the stirred emulsion through a

separating funnel, in the course of about 45 minutes. The stirring is continued for a further one hour when all the permanganate is consumed. Sufficient 10 per cent solution of sodium hydroxide is then added to make the solution alkaline. The mixture is filtered on a Büchner funnel and the manganese dioxide residue is washed with three 100 c.c. portions of hot water. The combined filtrate and washings are cooled and then acidified with concentrated hydrochloric acid. The precipitated piperonylic acid is filtered, washed and dried, m.p.  $225^{\circ}$  ; yield, 30 g.

**(b) Piperonylic acid chloride**

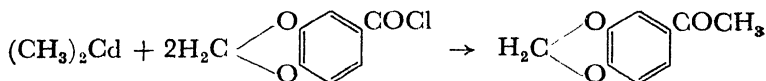
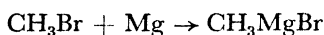
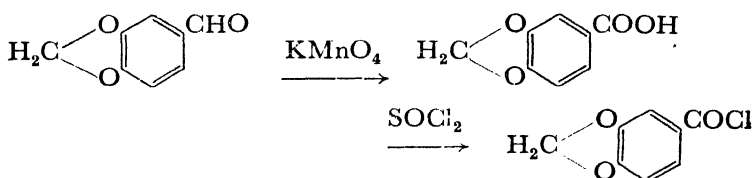
Piperonylic acid	... 30 g.
Thionyl chloride	... 30 c.c.

A mixture of 30 g. of piperonylic acid and 30 c.c. pure of thionyl chloride is refluxed for 3 hours on a water bath in a flask provided with a water-cooled condenser and calcium chloride guard tube. The excess thionyl chloride is removed by distillation under vacuum (water pump) and the acid chloride is distilled under vacuum. Yield, 25 g. B.P.  $155^{\circ}/25$  mm. It is a white solid ; m.p.  $80^{\circ}$ .

**(c) Acetopiperone**

In a flask provided with a dropping funnel, reflux condenser, mercury-sealed mechanical stirrer and two inlet tubes 6.25 g. of magnesium are suspended in 125 c.c. of dry ether; the flask being protected by a calcium chloride guard tube. Through one of the inlet tubes nitrogen gas (from a cylinder) which is passed through Fieser's solution and concentrated sulphuric acid is bubbled while through the other inlet tube a stream of methylbromide gas (dried by passing through a potassium hydroxide tower) is passed so as to bubble into the suspension which is well stirred. Ice cold water is circulated through the condenser. After all the methyl bromide (100 g.) has been passed through the solution this inlet is closed and the stirring continued for an additional 30 minutes. When all the magnesium has dissolved, the solution is cooled in ice and 24 g. of anhydrous cadmium chloride (dried to constant weight at  $110^{\circ}$ ) are added in 5 minutes. The mixture is stirred under reflux for about an hour. The ether is distilled off from the mixture on an electrical water bath. 60 c.c. of dry benzene are then added to the residue and about 25 c.c. of benzene are distilled off. 150 c.c.

of dry benzene are then added and the mixture is vigorously stirred. To the stirred mixture is added a solution of piperonylic acid chloride (25 g.) in 60 c.c. of dry benzene as rapidly as consistent with control of the exothermic reaction. The mixture is heated under reflux for an hour. It is then cooled to room temperature and decomposed with ice and sulphuric acid. The clear solution is transferred to a separating funnel and the benzene layer tapped off. The aqueous layer is extracted once with benzene (50 c.c.). The combined benzene extracts are washed once with 100 c.c. saturated sodium carbonate solution and then with saturated potassium chloride solution. It is then washed with water, and dried over anhydrous sodium sulphate. The benzene is then removed by distillation on a water bath. The residue is transferred to a 100 c.c. wide mouth conical flask and is cooled to room temperature. Then about 200 c.c. of petroleum ether (40-60°) are added to the flask and stirred. The material in the flask solidifies. It is filtered, washed with petroleum ether and dried in a vacuum desiccator; m.p. 85°; yield, 16 g.



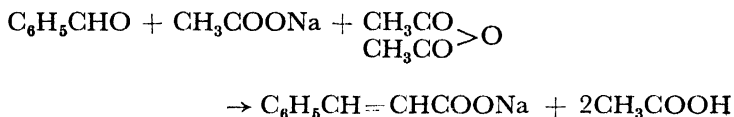
### Preparation 98

#### $\Delta$ -HYDRINDONE

##### (a) Cinnamic acid.

Benzaldehyde	... 10 g.
Acetic anhydride	... 15 g.
Sodium acetate (anhydrous)	... 5 g.

Freshly distilled benzaldehyde, acetic anhydride and freshly fused sodium acetate are introduced into a 250 c.c. round-bottom flask fitted with an air condenser. The flask is heated in an oil-bath kept at 180° for about 6 hours and continued the next day for another 3 hours. The condenser should be connected to a calcium chloride tube. The reaction mixture is poured while hot into a 500 c.c. round-bottom flask, made alkaline with sodium carbonate, diluted with water and steam-distilled till no more benzaldehyde passes over. The residue is filtered hot through a folded filter paper, cooled, and acidified with dilute hydrochloric acid. The precipitated cinnamic acid is purified by recrystallisation from hot water ; m.p. 133°. Yield, 7 g.



(b) **Hydrocinnamic acid.** ( $\beta$ -Phenylpropionic acid)

Cinnamic acid	... 10 g.
Caustic soda solution (N)	... 78 c.c.
Sodium amalgam (2½%)	... 170 g.

The cinnamic acid dissolved in the sodium hydroxide solution is introduced into a 250 c.c. dropping funnel and the sodium amalgam is added a little at a time and the liquid well shaken. The amalgam liquefies and hydrogen is evolved but only towards the end. When the whole of the amalgam has been added and bubbles of gas cease to be given off, the mercury is separated and the solution which contains the sodium salt of hydrocinnamic acid is transferred to a beaker and acidified when the free acid is precipitated as a colourless oil which slowly solidifies on cooling in ice and rubbing with a glass rod. The solid is filtered and recrystallised from plenty of warm water or from petroleum ether or chloroform. It crystallises in long colourless needles, m.p. 48·6°. Yield, 6-7 g.

(c)  **$\beta$ -Phenylpropionyl chloride**

Phenylpropionic acid	... 25 g.
Thionyl chloride (freshly distilled)	... 25 g.

The phenylpropionic acid dried overnight in a vacuum desiccator is dissolved in 15 c.c. of dry chloroform contained in a dry 500 c.c. round-bottom flask. Thionyl chloride is next weighed in and the flask is fitted with an efficient condenser carrying a calcium chloride tube. The reaction is started by gently warming and allowed to proceed overnight. Next morning the contents of the flask are heated on the water-bath to complete the reaction, and after cooling, transferred to a Claisen distilling flask. The flask is heated at  $100^{\circ}/30$  mm. till the thionyl chloride and chloroform are almost completely removed and the residue consisting chiefly of the acid chloride is fractionated. The portion coming over at  $125^{\circ}\text{--}135^{\circ}/35$  mm. is collected separately. Yield, 27 g.

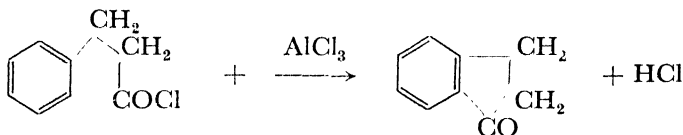
(d) **L-Hydrindone.**

$\beta$ -Phenylpropionyl chloride	... 20 g.
Aluminium chloride	... 20 g.
Petroleum ether (dried over sodium, b.p. $60\text{--}70^{\circ}$ )	... 60 c.c.

Freshly sublimed aluminium chloride ground up to a powder with petroleum ether (30 c.c.) is introduced into a dry 500 c.c. round-bottom flask. The acid chloride is dissolved in the remainder of the ether in a dry flask and transferred to a dry dropping funnel. The flask is fitted with a good cork carrying a reflux condenser. A doubly bored cork carrying a calcium chloride tube and a dropping funnel is fitted to the top of the condenser. The acid chloride solution is added from the dropping funnel a little at a time. The reaction shows a tendency to become vigorous so that the next addition has to be made only after the reaction slows down. When all the acid chloride has been added, the contents of the flask are heated on a water bath with constant shaking till the mixture boils and a rapid evolution of hydrogen chloride takes place. The flask is then lifted from the water-bath till the reaction subsides. The heating on the water-bath and subsequent cooling is repeated till there is very little evolution of gas. The homogeneous liquid separates into two layers, the lower layer being viscous and dark brown and the upper layer of petroleum ether practically colourless. Ice water (100 c.c.) is carefully added through the condenser to decompose the aluminium chloride addition compound and the flask is also cooled in ice-water during this process. The contents of the flask are now distilled in steam, the petroleum-



ether which passes over first, being collected in a distilling flask of a litre capacity, fixed by a cork to the condenser tube. The remainder is collected separately. Superheated steam at 140-150° hastens the process. The distillation is continued till the distillate is no longer milky. The distillate is saturated with sodium sulphate and shaken up in a one litre separating funnel with petroleum-ether to which some ether has been added. The aqueous layer is separated, and the petroleum-ether layer is washed with sodium carbonate solution and dried over anhydrous sodium sulphate. After removal of the petroleum-ether, the oily residue is poured into a crystallising basin which is cooled in ice. It solidifies to a mass of colourless crystals; m.p. 41°, b.p. 244°. Yield, 8 to 9 g.



### Preparation 99

#### CYCLOHEXANOL

(Catalytic hydrogenation by reduced nickel)

**Preparation of the catalyst.** A nickel cube weighing nearly 10 g. is dissolved in concentrated nitric acid. While the metal is dissolving, some kieselguhr (100-150 g.) is purified by boiling with concentrated nitric acid, washing with water, filtering and drying. The nickel nitrate solution is evaporated on a water-bath almost to dryness and taken up in about 50 c.c. of water. The nickel nitrate solution is mixed with the kieselguhr thoroughly in a nickel basin, evaporated to dryness and ignited on a Teclu burner till complete conversion into the oxide takes place and no brown fumes are evolved.

Alternatively, small pieces of pumice 2-3 mm. size, are boiled previously with dilute nitric acid, washed and dried. These pieces are impregnated with the nickel nitrate solution and dried with stirring on a water-bath. The impregnated pumice is

heated in a clean nickel crucible to a dull red heat till no further brown fumes are evolved.

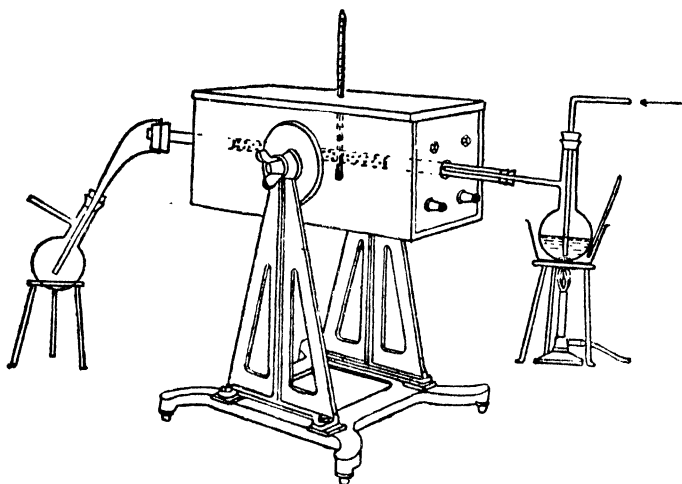
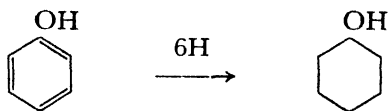


Fig. 44. Electric tube-furnace, with the nickel catalyst in the combustion tube for hydrogenation.

A combustion tube is loosely packed with this material which is kept in position by plugs of ignited asbestos wool. The packing is made in such a way that a length of about 10 inches is filled at the centre leaving an equal length free at each end. The combustion tube is introduced into an electric tube furnace (Fig. 44) the temperature of which is gradually raised to  $300\text{--}320^\circ$  and kept in this region by a regulation of the resistance connected in series with the heating element. The temperature is read by a thermometer pushed along with the combustion tube. Through one end of the tube hydrogen purified by passing through mercuric chloride solution and saturated permanganate solution, and dried by concentrated sulphuric acid and a tower packed with caustic soda pellets is passed rapidly. The gas is passed until no more water collects near the open end of the tube. This reduction takes nearly three hours. The reduced nickel is cooled in a current of hydrogen and if the experiment is to be carried out the following day the combustion tube is closed by tight fitting corks.

**Reduction.** Fifteen grams of phenol (freshly distilled) are introduced into a 100 c.c. distilling flask, fitted with a one-holed

cork carrying an L tube which to begin with is so adjusted as to be above the phenol layer. The side-tube of the distillation flask is fixed to the combustion tube by a tight fitting cork and is pushed in as far as possible. The combustion tube is heated to 190-200° and a rapid stream of dry hydrogen is passed as before to sweep out air, while a little later the L tube is pushed down into the layer of phenol. The distilling flask is heated to 170° by immersion in a glycerol bath, the temperature being kept at this point by adjusting the flame. The electric combustion furnace is tilted and the other end of the combustion tube is fitted with an adapter which goes into another distilling flask. The vapour of phenol should not be allowed to condense inside the tube. The hexahydrophenol condenses slowly and drops in the receiver. When all the phenol has volatilised over (2-3 hrs.), the tube is heated to 200° and finally cooled in a stream of hydrogen. The liquid that has collected is shaken up with ether, treated first with 50% caustic soda solution to remove phenol and then with saturated bisulphite to remove traces of cyclohexanone, finally with water and dried over anhydrous potassium carbonate. The ether is removed and the residual liquid fractionated, the portion boiling at 160-162° being collected. It has a pleasant aromatic odour, b.p. 161.5°; sp. gr. 0.96220°. Yield, 11 g.



### Preparation 100

#### O-PHTHALDEHYDIC ACID

##### (a) Phthalonic acid

Naphthalene	... 20 g.
Potassium permanganate	... 125 g. (in 1.25 litre)
Concentrated sulphuric acid	... 25 c.c.

20 g. of naphthalene, 125 g. of potassium permanganate and 1.25 litres of water are boiled together under reflux for 4 hours.

After leaving overnight, the solution is filtered from the manganese dioxide and some unchanged naphthalene, 25 c.c. of concentrated sulphuric acid are slowly added and the whole evaporated to dryness in a large basin. The dried residue is extracted with ether in a Soxhlet and the ether distilled off. The syrupy liquid which is left behind is cooled in ice and the separated crystals are collected at the pump, dissolved in the minimum quantity of water and filtered from a little undissolved phthalic acid. The solution, when evaporated on the steam bath, leaves a thick syrup which solidifies to a hard mass on cooling. It is powdered and dried in vacuum; m.p.  $115^{\circ}$ ; if anhydrous, m.p.  $144.5^{\circ}$ . Yield, 18 g.

**(b) The anil of phthalonic acid**

20 g. of phthalonic acid are dissolved in 100 c.c. of water and the solution heated on the water bath to  $60^{\circ}$ . 30 g. of freshly distilled aniline are stirred into the hot solution and the mixture heated for half an hour on the steam bath. Colourless prismatic crystals separate slowly. After standing for sometime at the room temperature, the crystals are filtered at the pump and dried in a vacuum desiccator, m.p.  $165^{\circ}$ . Yield, 30 g.

**(c) o-Carboxy-benzylideneaniline**

10 g. of the anil of phthalonic acid are taken in a perfectly dry flask fitted with an air condenser and a calcium chloride tube and 70 c.c. of dry xylene (prepared by drying the commercial xylene over sodium and distilling) are added and the mixture heated to boiling for an hour. On cooling, needle-shaped crystals separate out. These are filtered and dried, m.p.  $174^{\circ}$ . Yield, 6 g.

**(d) o-Phthalaldehydic acid**

5 g. of o-carboxy-benzylideneaniline are boiled for half an hour with 50 c.c. of 10 per cent hydrochloric acid. On cooling, flaky crystals of the acid are thrown down, m.p.  $99-100^{\circ}$ . Yield, 2 g.

**Alternative**

A solution of phthalonic acid (15 g.) in 20 c.c. of water is treated with a freshly prepared solution of sodium bisulphite, and the mixture evaporated to dryness on the water-bath. The residue is stirred into 50 c.c. of concentrated hydrochloric acid and evaporated to dryness on the water-bath. The process is repeated and the residue extracted with benzene in a Soxhlet. After distilling the benzene on a water-bath, the crystalline product

weighing 9 to 10 g., is dissolved in 30 c.c. of 2N-NaOH by boiling. The alkaline extract is filtered, cooled and acidified with dilute hydrochloric acid. The crystalline precipitate that separates is filtered after 20 minutes and washed with a small quantity of ice-cold water. The substance softens at 94° and melts to a clear liquid at 96°. Yield, 8 g.

### Preparation 101

#### L-PHENYLINDOLE

Acetophenone	... 10 g.
Phenylhydrazine	... 9 g.
Rectified spirits	... 40 c.c.
Anhydrous zinc chloride	... 62.5 g.

A mixture of 10 g. of acetophenone and 9 g. of phenylhydrazine is warmed on a boiling water bath for 1 hour. After addition of 40 c.c. of rectified spirits, the hot mixture is allowed to cool in ice. Acetophenone phenylhydrazone precipitates. It is filtered and washed with 10 c.c. of alcohol and dried for half an hour in a vacuum desiccator over anhydrous calcium chloride. Yield, 14 g. ; m.p. 105-106°.

14 g. of acetophenone phenylhydrazone are mixed well with 62.5 g. of anhydrous zinc chloride in a mortar, the mixture is placed in a 500 c.c. wide-mouth round-bottom flask and heated in an oil bath at 170°, the mixture being stirred vigorously by hand. In about a few minutes the entire mass melts and dense white fumes are evolved. The flask is then removed from the oil-bath and the stirring continued for another 5 minutes. Then 50 g. of clean white sand are added with stirring to prevent the contents of the flask solidifying to a hard mass. 200 c.c. water and 6 c.c. of concentrated hydrochloric acid are then added to the flask and the flask is heated for 10 hours on a water bath. The zinc chloride goes into solution. The sand and the crude 2-phenylindole are then filtered off, and the residue boiled with 200 c.c. of rectified spirits. The hot mixture is treated with a little norit and filtered through a preheated Büchner funnel ; the residue is washed with 20 c.c. of hot rectified spirits. The combined filtrates are cooled to room temperature when the 2-phenylindole crystallises

out. It is filtered, washed twice with 10 c.c. portions of cold alcohol and then dried over anhydrous calcium chloride in a vacuum desiccator. Yield, 8 g. ; m.p. 188-189°.

### Preparation 102

#### Ⓐ-METHYLINDOLE

Phenylhydrazine	... 10 g.
Acetone	... 6 g.
Zinc chloride (anhydrous)	... 70 g.

The phenylhydrazine and acetone are mixed in a 100 c.c. round-bottom flask when the mixture becomes warm with separation of a good deal of water. The mixture is heated on a water-bath for 15 minutes and the progress of the reaction is tested by Fehling's solution, acetone being added so long as reduction is observed. The turbid oil (acetone-phenylhydrazone) is placed in a big copper crucible and the excess of acetone removed by heating on the water-bath. The zinc chloride is then added and the mixture heated for fifteen minutes on the water-bath with continuous stirring. Finally the crucible is heated in an oil bath at 180°, and after the contents have become completely dark, the crucible is quickly removed, the contents treated with 3½ times its weight of hot water, acidified with a little hydrochloric acid and steam distilled. A pale yellow oil comes over slowly and gradually solidifies. The solid is melted to free it from water and distilled under reduced pressure. It is obtained as pale yellow crystals, with a foul smell, m.p. 95°, b.p. 272 /750 mm. Yield, 6 g.

### Preparation 103

#### COLLIDINE

This preparation involves a series of intermediate compounds commencing with the condensation of ethyl acetoacetate and aldehyde-ammonia.

#### (a) **3 : 5-Dicarbethoxy-1 : 4-dihydrocollidine.**

26 g. of freshly-distilled ethyl acetoacetate and 6.5 g. of a good crystalline specimen of aldehyde-ammonia are mixed in a 100 c.c. beaker and warmed gently for about five minutes at 100—

110°, the liquid being kept stirred by a thermometer. An equal volume of dilute hydrochloric acid is added with stirring, to the hot liquid and the mixture is stirred until the oil which separates sets to a hard solid mass. This is powdered, filtered, washed first with very dilute hydrochloric acid and finally with water. A small portion (1 g.) may be recrystallised from hot alcohol and the rest used for the succeeding preparations. It is obtained in colourless plates with a bluish fluorescence, m.p. 131°. Yield, 15 g.

**(b) 3 : 5-Dicarbethoxycollidine.**

The crude dihydrocollidine dicarboxylate is dissolved in an equal weight of alcohol in a 125 c.c. conical flask which is immersed in ice-cold water and oxidised by nitrous fumes generated by the action of concentrated nitric acid on lumps of arsenious oxide. Before passing the gas into the solution it is better to pass it through an empty wash-bottle. The gas is passed till a test sample dissolves to a clear solution in dilute hydrochloric acid. The alcohol is evaporated off on a water-bath, the residue treated with sodium carbonate solution till alkaline and the oil which separates is extracted with ether. The ether extract is dried over anhydrous potassium carbonate and the ester recovered as usual. The fraction passing over between 290-310° is collected separately and redistilled, the pure ester distilling between 308-310°. It is obtained as a yellow oil, b.p. 308-310°. Yield, 10 g.

**(c) Potassium salt of 3 : 5-dicarboxycollidine.**

10 g. of the ester are refluxed on a water-bath with about 10 times the volume of alcoholic potash (3N) for 4 hours. The alcoholic solution is decanted from the potassium salt which is deposited as a white crystalline crust. From the alcoholic solution a further yield of the salt is obtained by adding an equal volume of ether. The total product is washed with alcohol, then with ether and dried in the steam oven. It is obtained as a white crystalline mass. Yield, 10 g.

**(d) Collidine.**

10 g. of the dry powdered potassium salt obtained in (c) are mixed well with 20 g. of good slaked lime and the mixture introduced into a combustion tube 60 cm. long sealed at one end. After introducing the mixture, a further layer of 5 cm. of slaked lime

is added and the combustion tube drawn out to form a condenser. The combustion tube is heated in a furnace commencing at the closed end and heating the rest gradually. Finally the entire tube is heated as strongly as possible. The distillate is extracted with ether, dried over solid caustic potash and worked up to give the base, employing all the precautions necessary for work with small quantities of substances. The fraction between  $169-174^{\circ}$  is collected. It is a greenish-yellow liquid with an obnoxious odour, b.p.  $172^{\circ}$ . Yield, 2 g.

### Preparation 104

#### QUINOLINE

##### (Skraup's synthesis, modification)

Aniline	... 19 g.
Nitrobenzene	... 140 g.
Boric acid	... 12.5 g.
Glycerol	... 75 c.c.
Ferrous sulphate (crystals)	... 7 g.

The boric acid is dissolved in the glycerol and cooled. In a 500 c.c. round bottom flask, the ferrous sulphate, aniline and nitrobenzene are taken in order and the cooled glycerol-boric acid mixture is then added. The mixture is stirred well and concentrated sulphuric acid (35 c.c.) added. The contents of the flask are heated under reflux, at first carefully and then kept boiling gently for 5 hours. The product is diluted with water and distilled in steam to remove nitrobenzene. The residue is rendered alkaline with about 125 c.c. of 60% sodium hydroxide solution and distilled again in steam using a litre round-bottom flask. The distillate which is a mixture of unreacted aniline along with quinoline is extracted with ether, the ether extract dried over anhydrous potassium carbonate and the ether removed by distillation. The mixture of quinoline and aniline is then refluxed with 5 c.c. of acetic anhydride for 15 minutes to acetylate aniline. The reaction product is then rendered alkaline with potassium carbonate and steam-distilled once again. The distillate which now contains only quinoline is extracted with ether, the ether extract dried over solid sodium hydroxide and the quinoline distilled after removal



of ether. It is a colourless liquid with a disagreeable odour  
b.p.  $237^{\circ}$  ; yield, 17 g.

### Preparation 105

#### 8-HYDROXYQUINOLINE

o-Nitrophenol	... 6 g.
o-Aminophenol	... 8 g.
Glycerol (Anhydrous)	... 18 g.
Sulphuric acid (concentrated)	... 16 g. (9 c.c.)

#### Preparation of anhydrous glycerol.

Commercial glycerol (25 g.) is heated in a 10 cm. porcelain basin carefully over a wire gauze on a free flame while stirring continuously with a thermometer till the temperature rises to  $180^{\circ}$ . It is then cooled to  $100^{\circ}$  and poured into a wide-mouthed bottle and kept in a desiccator over sulphuric acid.

#### 8-Hydroxyquinoline

The nitrophenol, aminophenol, and the glycerol are introduced into a litre round-bottom flask. The sulphuric acid is added slowly while mixing thoroughly with a glass rod and cooling the flask under the tap. The mixture is then heated in an oil-bath to  $150^{\circ}$ , after fitting the flask with a Liebig condenser. If the reaction becomes vigorous, the flask is lifted out of the bath. After the reaction has slowed down, heating is continued for five hours, keeping the contents gently boiling. After cooling, a little water is added and the mixture is steam-distilled to remove the unreacted nitrophenol. A solution of sodium hydroxide (12 g. in 100 c.c. water) is added to the residue in the flask and then solid sodium carbonate little by little till alkaline and the mixture again steam-distilled. The 8-hydroxyquinoline passes over slowly and solidifies sometimes in the condenser tube, in which case the cooling water is removed momentarily to melt it and renewed soon after. Nearly 600 c.c. of the distillate are collected. The solid is filtered and recrystallised from plenty of water, using norit, and filtering under suction, and transferring the filtrate to a beaker. The crystals are filtered off and dried *in vacuo*. Colourless needles melting at  $76^{\circ}$  are obtained. Yield, 8 g.

**Preparation 106****QUINALDINE**

Aniline	... 15.5 g.
Concentrated hydrochloric acid	... 30 c.c.
Paraldehyde (fresh)	... 22.5 c.c.

The aniline is introduced into a litre round bottom flask and the hydrochloric acid added dropwise with external cooling of the flask in an ice bath. Paraldehyde is then added and the mixture stirred well mechanically. The flask is fitted with a Liebig condenser and left at room temperature. The condensation takes place gradually with a slight evolution of heat. The liquid is then boiled under reflux for 3 hours, cooled, made alkaline with sodium hydroxide and steam distilled. From the distillate the crude base is extracted twice with ether (50 c.c.) the ether extract dried over solid potassium hydroxide or anhydrous potassium carbonate. The ether is removed by distillation and the unchanged aniline and secondary bases are removed by boiling under reflux for 15 minutes with 5 c.c. of acetic anhydride. The contents are cooled, rendered alkaline with a saturated solution of sodium carbonate and steam-distilled. From the cooled distillate, the quinaldine is extracted with ether, the ether extract dried over caustic potash, and after removal of ether is purified by distillation preferably in vacuum. Yield, 10 g. B.P. 244°/760 mm.

**Preparation 107**

**1 : 2 : 3 : 4-TETRAHYDRO-1-METHYL-6 : 7 METHYLENEDIOXY-  
ISOQUINOLINE**

Piperonal	... 20 g.
Malonic acid	... 22 g.
Pyridine	... 13 c.c.
Piperidine	... 8 drops

**(a) 3:4-Methylenedioxycinnamic acid.**

Piperonal, malonic acid, pyridine and piperidine are heated together on a boiling water-bath for 2 hours and then for 15 minutes over a free flame. The contents of the flask are then treated

with excess of dilute hydrochloric acid and the solid filtered off. M.P. 247°. Yield, 22 g.

(b)  **$\beta$ -3 : 4-Methylenedioxyphenylpropionic acid.**

22 g. of the uncrystallised acid are dissolved in the requisite amount of 10 per cent. sodium hydroxide and treated with 300 g. of 4 per cent sodium amalgam gradually. Dilute hydrochloric acid is simultaneously added little by little to neutralise most of the alkali as it is formed. After keeping for an hour, the mercury is tapped off, the solution filtered from any dirt, and acidified with concentrated hydrochloric acid after cooling in ice. M.P. 87°. Yield, 17 to 18 g.

(c)  **$\beta$ -3 : 4-Methylenedioxyphenylpropionamide.**

The acid (17 g.) is dissolved in 55 c.c. of dry chloroform and allowed to react at the room temperature for 5 hours with 12 c.c. of freshly distilled thionyl chloride. The product is then poured into a solution containing 250 c.c. of liquor ammonia and 7.5 g. of caustic soda and shaken well. The chloroform layer is separated and on distilling off the chloroform, the amide remains as a crystalline solid; m.p. 122°. Yield, 14 g.

(d)  **$\beta$ -3 : 4-Methylenedioxyphenylethylamine (Homopiperonylamine).**

The amide (14 g.) is finely powdered and suspended in 130 c.c. of water and then poured into a solution of sodium hypobromite prepared from 130 c.c. of 25 per cent NaOH and 13.5 g. of bromine. The solution is kept at 70° for an hour, treated with 40 g. sodium hydroxide pellets, for a further 15 minuter at 80°, cooled and extracted with ether. The ether extract is dried over potassium carbonate, the ether evaporated and the amine distilled under reduced pressure. B.P. 145°/10 mm. Yield, 6.5 g.

(e) **3 : 4-Dihydro-1-methyl-6 : 7-Methylenedioxyisoquinoline.**

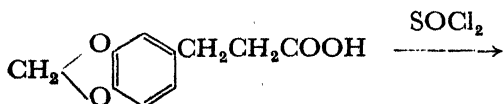
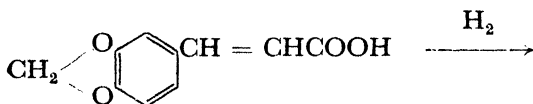
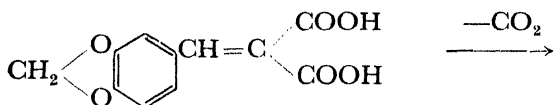
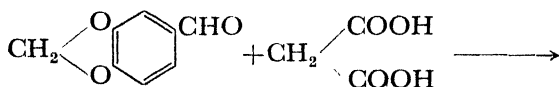
6 g. of homopiperonylamine are dissolved in 30 c.c. of dry ether and treated with 4.2 g. of acetic anhydride which is added drop by drop. The acetyl derivative of the amine is thus formed. The ether is then distilled off and the residual oil treated with 30 c.c. of phosphoryl chloride. The solution is heated on a boiling water-bath for 2 hours, cooled, and poured on to crushed ice. The acidic solution is filtered from any tarry matter, cooled in ice and made alkaline with caustic soda. The base separates as an oil and is extracted completely with ether.

The ether extract is shaken with 45 c.c. of 4N sulphuric acid (3 lots of 15 c.c. each), the acid extract made alkaline and again extracted with ether. The ether extract is dried over potassium carbonate and the ether distilled off. The isoquinoline derivative is left behind as a crystalline solid which is dried on a porous plate. M.P. 92°. Yield, 4.8 g.

On rubbing with concentrated hydrochloric acid, it forms a crystalline hydrochloride, m.p. 240°. The picrate melts at 230°.

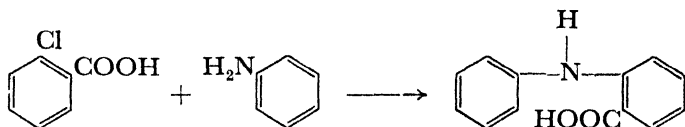
**(f) 1 : 2 : 3 : 4-Tetrahydro-1-methyl-6 : 7-methylnenedi-oxyisoquinoline.**

3.2 g. of the dihydroisoquinoline are dissolved in 40 c.c. of 4N sulphuric acid and heated for 2 hours on the boiling water-bath with 4 g. of zinc dust. The hot solution is filtered from the zinc, cooled, made alkaline with strong ammonia and the base extracted thrice with benzene (3 lots of 10 c.c. each). The benzene extract is shaken with dilute sulphuric acid, the acid extract again made alkaline and extracted with benzene in the same way. The benzene extract is finally dried over potassium carbonate and the benzene distilled off. The tetrahydrobase is left behind as an oil. Yield, 2.4 g. It forms a hydrobromide, m.p. 232° and a picrate, m.p. 191°.





The above mixture is boiled in a round-bottom flask of 250 c.c. capacity fitted with a short air condenser so that some water escapes from the top of the condenser. The reaction is over in three hours and the mixture becomes dark. The unreacted aniline is removed by steam distillation and the residue filtered hot. The filtrate is once again boiled with norit and filtered. On adding concentrated hydrochloric acid to the hot filtrate, phenylanthranilic acid is precipitated. This is filtered when cold, washed with cold water and dried. One gram is recrystallised from a mixture of acetic acid and alcohol. The rest is used for the next preparation. It crystallises in rhombic plates, m.p. 183-184° Yield, 13 g.



#### (b) Acridone

Phenylanthranilic acid	... 10 g.
Concentrated sulphuric acid	... 70 g.

The mixture of the two is heated in a round-bottom flask on a water-bath for three to four hours. The yellowish-green fluorescent solution is poured into a beaker, cooled in ice and diluted with 80 c.c. of ice water which is added slowly with vigorous shaking and cooling. The yellow precipitate of acridone is filtered, warmed in a big basin with 600 c.c. of 2½ per cent sodium carbonate to remove any unchanged phenylanthranilic acid and again filtered. It is washed with water, dried on a porous plate and a sample recrystallised from glacial acetic acid. Yellow needles. Yield, 8 g.

#### (c) Acridine

4 g. of acridone are well mixed with good zinc dust (15 g.) and introduced into a hard glass tube 12 in. long closed at one end. An additional layer of 10 g. of zinc dust is added, the open end is fitted with a bent tube and the closed portion containing the mixture is heated commencing with the zinc layer and gradually extending it to the mixture. The acridine formed

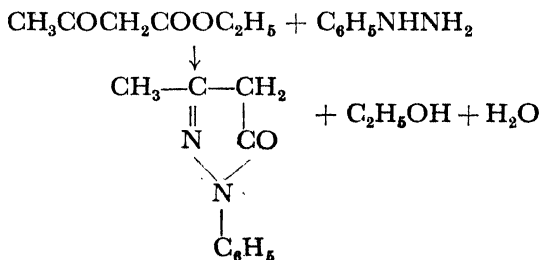
on reduction sublimes towards the open end of the tube and has a pink colour. The sublimate is dissolved in hydrochloric acid, filtered and the acridine precipitated by addition of alkali. It is filtered and recrystallised from methyl alcohol with the addition of a little decolourising charcoal. It crystallises in bright yellow needles, m.p.  $110^{\circ}$ . Yield, 2 g.

### Preparation 109

#### 3-METHYL-1-PHENYLPYRAZOLONE

Acetoacetic ester	... 13.5 g.
Phenylhydrazine	... 10 g.

The acetoacetic ester (freshly distilled) and the phenylhydrazine are introduced into a 100 c.c. flask which is corked and vigorously shaken. The oil that is formed is heated on a water bath for an hour or two until a test portion crystallises on adding acetone. Acetone (20 c.c.) is added and the mixture allowed to crystallise. The crystals are washed with ether and dried at  $100^{\circ}$ . The product is recrystallised from hot aqueous alcohol. It comes out in white crystals, m.p.  $127^{\circ}$ . Yield, 16 g.



### Preparation 110

#### 2-AMINOPYRIDINE

Pyridine (dry)	... 25 g.
Toluene (dry)	... 75 c.c.
Sodamide	... 19 g.

75 g. of anhydrous sulphur-free toluene and 19 g. of granular sodamide are placed in a 500 c.c. three-necked flask fitted with a mercury-seal mechanical stirrer, reflux condenser, thermometer and inlet tube for nitrogen. The stirrer is set in motion, a steady stream of nitrogen is bubbled through the toluene, and the flask is heated in an oil-bath at about 130-140° so that the temperature in the reaction flask is maintained at 110°. 25 g. of pure dry pyridine is then added dropwise in the course of an hour through the condenser. After sometime, the reaction mixture turns black and then viscous and frothing occurs due to liberation of hydrogen. When all the pyridine has been introduced, the heating is continued for a further period of 5 hours while the internal temperature of the reaction flask is maintained at 110°. Towards the end of the reaction, stirring becomes difficult owing to the separation of a solid or viscous cake. The stirring is discontinued and passage of nitrogen stopped and the reaction mixture is allowed to cool. Then water (50 c.c.) is added dropwise through the condenser over a period of an hour while nitrogen is being once again bubbled through the flask and stirring commenced. During the addition of water, the temperature rises to 50°. The contents of the flask are then transferred to a separating funnel and the lower aqueous layer separated. It is extracted twice with toluene (40 c.c.). The toluene extracts are added to the main toluene layer and the toluene is dried over anhydrous potassium carbonate for 2 hours. The toluene is then filtered into a dry distilling flask and the toluene removed by distillation. The syrupy residue left in the flask is purified by distillation under reduced pressure from an oil-bath maintained at 120-130°. 2-Aminopyridine distils at 95°/10 mm. It solidifies on cooling to a colourless solid; m.p. 55°. Yield, 20 g.

### Preparation 111

#### CAFFEINE FROM TEA

Tea	... $\frac{1}{4}$ lb.
Lead acetate	... 20 g. in 100 c.c. water
Litharge	... 20 g.

600 c.c. of water are taken in a litre round-bottom flask, the tea (fluff or dust) added and the contents boiled for half an



hour on a wire gauze. Meanwhile basic lead acetate is prepared by boiling the lead acetate solution with litharge with continuous stirring. The solution is filtered and heated on a boiling water-bath. The tea infusion is next filtered through cotton cloth, the flask is washed and the infusion poured back into the flask. The basic lead acetate is added little by little till no further precipitation of tannin takes place. The mixture is heated to boiling, filtered and the precipitate washed with 100 c.c. of hot water. The excess of lead is removed as sulphate by adding dilute sulphuric acid drop by drop and after allowing the precipitate to settle, the clear liquid is decanted and concentrated to 300 c.c. This is then boiled with 0.5 g. of norit and filtered hot. After cooling, the filtrate is extracted with 50 c.c. of chloroform thrice, the chloroform distilled from the combined extract and the residue boiled up with 50 c.c. of water or more and a little norit, if still coloured. The solution is filtered hot and concentrated to 10 c.c. and set aside to crystallise. The caffeine comes out slowly as white crystals of a mixture of the anhydrous and the hydrated forms. This may be further purified by vacuum sublimation. M.P. of hydrate, 132-133°; anhydrous 237°. Yield, 1-2 g.

## Preparation 112

### MESCALINE

#### 3 : 4 : 5-Trimethoxyphenylethyl amine

##### (a) Trimethylgallic acid

Gallic acid	... 55 g.
Dimethyl sulphate	... 150 c.c.

A solution of 55 g. of gallic acid in sodium hydroxide solution (90 g. of sodium hydroxide in 500 c.c. water) is placed in a 2 litre three-neck flask fitted with a mercury-seal stirrer, a dropping funnel and a two-holed rubber cork carrying a thermometer and a Bunsen valve. 75 c.c. of dimethyl sulphate are added dropwise with stirring, maintaining the temperature below 35°. After 30 minutes, another 75 c.c. of dimethyl sulphate are added dropwise, keeping the temperature below 40°. The stirring is continued for a further 30 minutes and the solution is then heated under reflux for one

and a half hours. A solution of 25 g. of sodium hydroxide in 50 c.c. water is added and the solution refluxed for a further two hours. The solution is cooled and acidified with concentrated hydrochloric acid and the precipitated acid is filtered, washed with ice water and dried at 80°. M.P. 155°. Yield, 55 g.

**(b) 3 : 4 : 5-Trimethoxybenzoyl chloride**

3 : 4 : 5-Trimethoxybenzoic acid ... 55 g.

Phosphorus pentachloride ... 55 g.

The acid obtained in the previous step is thoroughly dried in a vacuum and treated with 55 g. of phosphorous pentachloride in a 250 c.c. round-bottom flask fitted with an air condenser (calcium chloride guard tube). The mixture is heated on a water-bath for one hour. The phosphorous oxychloride formed is then removed by distilling *in vacuo* and the acid chloride then distilled at 5 mm. The liquid distilling over (130°/5 mm.) solidifies immediately. The acid chloride is redistilled to yield a colourless product. Yield, 40 g.

**(c) 3 : 4 : 5-Trimethoxybenzaldehyde (Rosenmund reduction)**

A solution of 40 g. of the foregoing acid chloride in 200 c.c. of pure dry xylene is placed in a three-necked flask equipped with a mercury seal stirrer, a gas inlet tube and a reflux condenser (guard tube). The experiment is best conducted inside a fume cupboard. A layer of paraffin oil over the mercury in the seal prevents mercury which retards the reaction, from splashing into the vessel. 10 g. of 3% palladised barium sulphate are added and a stream of hydrogen from a Kipp purified by passing through solutions of potassium permanganate, lead acetate and concentrated sulphuric acid is passed rapidly through the mixture which is kept vigorously stirred, and heated to about 145-155° by an oil-bath. Evolution of hydrogen chloride begins almost immediately and is over in about three to five hours. The solution is then filtered from the catalyst and the solvent is removed *in vacuo*. The residue is transferred to a smaller flask and distilled at 0.1 mm. A pre-run of 1 : 2 : 3-trimethoxybenzene is collected below 105°. The aldehyde distils between 105-110° and immediately solidifies to a colourless solid, m.p. 70-75°. Yield, 22 g.

**3 : 4 : 5-Trimethoxynitrostyrene**

11 g. of the foregoing aldehyde are dissolved in 45 c.c. of glacial acetic acid and 11 c.c. of nitromethane and 4.5 g. of ammonium acetate are added. After refluxing gently for one hour, the solution is cooled and poured on to 150 g. of crushed ice. The crude nitrostyrene is filtered and recrystallised from the minimum amount of alcohol, yielding 8 g. of yellow crystals, m.p. 120°.

**3 : 4 : 5-Trimethoxyphenylethylamine**

5 g. of lithium aluminium hydride and 200 c.c. of absolute ether are placed in a 1 litre three-necked flask fitted with a mechanical stirrer (mercury seal), an efficient condenser (calcium chloride guard tube) and a dropping funnel. A solution of 8 g. of 3 : 4 : 5-trimethoxynitrostyrene in 25 c.c. of pure tetrahydrofuran and 25 c.c. of absolute ether is dropped in at such a rate that there is only gentle reflux of the ether. The mixture is stirred for a further hour after completion of addition and left overnight. The excess lithium aluminium hydride is then decomposed by the careful addition first of moist ether (200 c.c.) and then water. The addition of water is stopped just at the moment when the inorganic hydroxides form a pasty mass sticking to the sides of the flask. The ether solution is then decanted off and the inorganic residue washed with more ether. The ether is then removed on a water-bath and the residue distilled at 5 mm. 3 : 4 : 5-Trimethoxyphenylethylamine collects at 150-155°/5 mm. Yield 4.5 g.

**Preparation 113****L-OPIANIC ACID**

Narcotine	... 10 g.
Manganese dioxide	... 18 g.
Concentrated sulphuric acid	... 9 c.c.

10 g. of powdered narcotine are dissolved in 150 c.c. of water containing 9 c.c. of concentrated sulphuric acid. The solution is heated under reflux for 30 minutes. 18 g. of powdered manganese dioxide are added in small quantities at a time, taking care that the liquid does not froth over. The mixture is heated for another 10 minutes and the flask is then allowed to stand for 12 hours.

The contents of the flask are then filtered and the residue consisting of a mixture of the acid and excess of manganese-dioxide is transferred to a beaker, 100 c.c. of water are added, the mixture boiled and filtered through a hot-water funnel. The opianic acid crystallises out slowly in soft feathery needles, m.p. 148°. Yield, 4 g.

### Preparation 114

#### PREPARATION OF COTARNINE FROM NARCOTINE

Narcotine	... 20 g.
Concentrated nitric acid	... 40 c.c.

100 c.c. of water are added to 40 c.c. of strong nitric acid (sp. gr. 1.42) and the solution warmed to 50°. To this warm solution, 20 g. of powdered narcotine are added in small quantities at a time, the whole addition requiring half an hour. The orange coloured solution is left overnight, filtered and cooled well in ice. Strong caustic soda solution (30 g. in 40 c.c. water) is added slowly with stirring. Cotarnine separates out as a yellow crystalline precipitate. The solid is filtered after half an hour, washed with cold water and dried in a desiccator. M.P. 130-132°. Yield, 9.8 g.

The filtrate on acidifying and keeping, yields 1 to 2 g. of opianic acid.

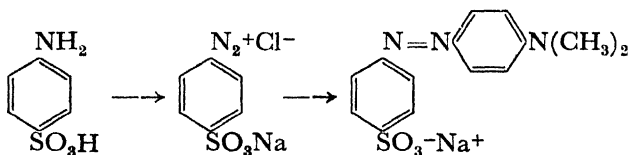
**Crystallisation of cotarnine.** 10 g. of crude cotarnine and 100 c.c. of benzene dried over sodium are heated on a water-bath under reflux. The flask is frequently shaken and the hot supernatant liquid is filtered through a fluted filter paper. More benzene is added to the undissolved portion and again heated. This operation is repeated till the whole of the substance is dissolved. The benzene solution, on standing, deposits yellow needles, m.p. 132°. Yield, 6 g. The mother liquor on concentration leaves behind nearly 3 g. of slightly impure cotarnine, m.p. 129-132°.

### Preparation 115

#### METHYL ORANGE

Sodium carbonate (anhydrous)	... 4 g.
Sulphanilic acid	... 12 g.
Sodium nitrite	... 4.6 g. (in 20 c.c. water)
Dimethylaniline	... 8 g.

The sodium carbonate is dissolved in 150 c.c. of water contained in a litre beaker. The sulphanilic acid is added and the beaker warmed to bring it into solution. The beaker is cooled in ice and the sodium nitrite dissolved in 20 c.c. of water is added. A mixture of concentrated hydrochloric acid (8 c.c.) and water (10 c.c.) is then added slowly so that the temperature does not rise above  $5^{\circ}$ . To the solution of the diazonium salt thus prepared an ice-cold solution of the dimethyl aniline in dilute hydrochloric acid (8 c.c. strong acid diluted with 25 c.c. of water) is added. The mixed solution is made alkaline with sodium hydroxide and the dye salted out by adding about 30 g. of common salt. After keeping for an hour the sodium salt is filtered, washed with a little ice-water and recrystallised from boiling water. Yield, 20 g.



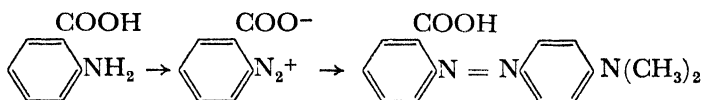
### Preparation 116

#### METHYL RED

Anthranilic acid	... 5 g.
Concentrated hydrochloric acid	... 15 c.c.
Sodium nitrite	... 2.5 g.
Dimethyl aniline (freshly distilled)	... 4.65 g. (5 c.c.)
Sodium acetate	... 50 g.

Into a 250 c.c. beaker, 150 c.c. of water are measured, the hydrochloric acid is added first and then the anthranilic acid. The mixture is stirred till solution is complete, cooled in ice and then diazotised by adding in small portions the solid nitrite. The solution is kept in ice for half an hour. Meanwhile the dimethyl aniline is dissolved in 50 c.c. of water containing 5 c.c. of concentrated hydrochloric acid, in a tall beaker of 600 c.c. capacity. The diazonium salt is poured into this solution and the sodium acetate

added immediately. The mixture is warmed to 40°C. on a water-bath, when the red dye separates quickly. After an interval of three hours by which time the reaction is complete, the dye is filtered, washed with water freely as it is insoluble, and air-dried. It is rather difficult to crystallise. Yield 8 g.



### Preparation 117

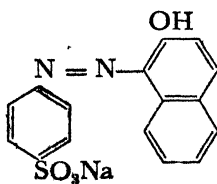
#### ORANGE II

Sulphanilic acid ... 5.3 g.

$\beta$ -Naphthol. ... 3.6 g.

5.3 g. of sulphanilic acid are diazotised as described earlier. The cold diazonium solution is added with stirring to a solution of 3.6 g. of  $\beta$ -naphthol in 20 c.c. of 10 per cent sodium hydroxide solution. The mixture is stirred for about 10 minutes after the completion of the addition and then heated to bring about dissolution of the pasty mass. 10 g. of sodium chloride are then added and the solution warmed to dissolve the salt. The dye which crystallises on cooling to room temperature is filtered and washed with a little saturated salt solution and dried at 80°.

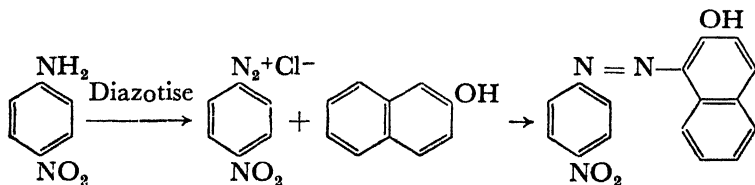
Further purification of the dye may be effected by dissolving it in the minimum quantity of boiling water, allowing to cool to 80° and adding twice the volume of rectified spirits. The pure dye which crystallises out is filtered, washed with alcohol and dried in air. Yield, 7 g.



**Preparation 118***p*-NITROBENZENE-AZO- $\beta$ -NAPHTHOL

<i>p</i> -Nitraniline	... 7 g.
Concentrated Sulphuric acid	... 15 c.c. (diluted with 15 c.c. of water)
Sodium nitrite	... 3.5 g. (in 25 c.c. of water)
Sodium acetate	... 7 g. (in 15 c.c. of water)
$\beta$ -Naphthol	... 7.5 g. (in 40 c.c. of 10% caustic soda).

The *p*-nitraniline is mixed with the diluted acid in a 250 c.c. beaker and cooled in a freezing mixture of ice and salt. The nitrite solution is added slowly and carefully from a dropping funnel. At first the *p*-nitraniline dissolves, and a pasty mass of the diazo compound separates soon after. The sodium acetate solution is now added, and the solution of  $\beta$ -naphthol in alkali is diluted to 100 c.c. in a 600 c.c. beaker. The diazo solution is now poured in, with stirring. Coupling takes place and a scarlet precipitate of the dye is obtained. After keeping for about ten minutes, the dye is filtered at the pump, washed with hot water and dried. Yield 10 g.

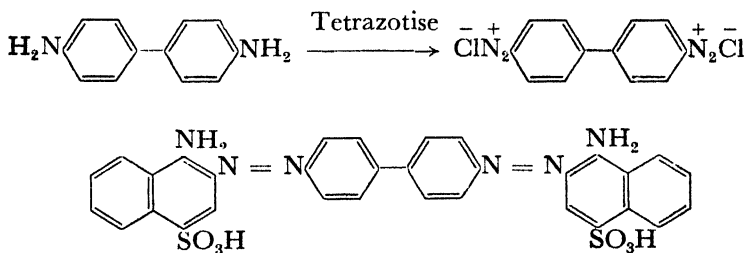
**Preparation 119**

## CONGO RED

Benzidine	... 4.6 g.
Sodium nitrite	... 3.5 g. (100%)
Sodium naphthionate	... 16 g.

4.6 g. of benzidine are dissolved in a hot mixture of 12 c.c. of concentrated hydrochloric acid and 100 c.c. of water. The solution is cooled in an ice bath to 0-5° and treated with a solution of 3.5 g. of sodium nitrite in 25 c.c. of water during two minutes with

good stirring. After five minutes, the 'tetrazo' solution is added to a solution of 16 g. sodium naphthionate and 20 g. crystallised sodium acetate in 250 c.c. of water. The mixture is stirred well and let stand for one hour. The coupling is complete, when a test portion on warming with hydrochloric acid does not evolve nitrogen. The blue-black precipitate of the dye acid is dissolved by the gradual addition of sodium carbonate (about 10 g.) followed by stirring and warming to 80°. The hot solution is filtered, the filtrate just saturated with sodium chloride, allowed to cool to room temperature and then cooled in ice. The congo red is filtered and washed with saturated solution of sodium chloride and dried in air ; yield 30 g.



### Preparation 120

#### MALACHITE GREEN

Dimethylaniline	... 18 g.
Benzaldehyde	... 7 g.
Concentrated hydrochloric acid	... 16 g.

Freshly distilled dimethylaniline, benzaldehyde and concentrated hydrochloric acid are introduced into a litre round bottom flask fitted with a water-cooled condenser and heated for about 14 hours. The reaction product is rendered alkaline with caustic soda and distilled in steam to remove the unreacted benzaldehyde and dimethylaniline. The residue is poured into 500 c.c. of water and the leuco base is obtained in the form of granules. It is filtered and washed free from alkali and dried at 100°. It is recrystallised from boiling alcohol.

The leuco base is converted into the dye by oxidation. 10 g.

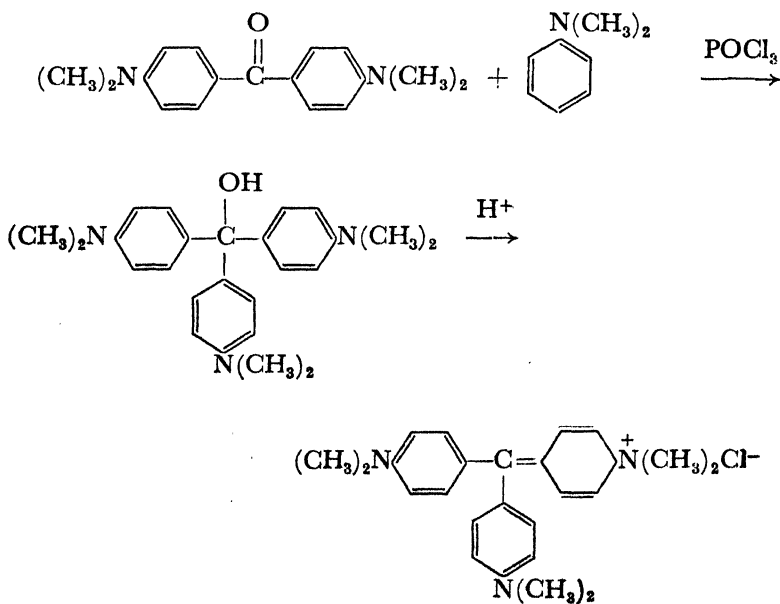


$$\begin{array}{c}
 \text{CHO} + 2 \text{N(CH}_3)_2 \longrightarrow \text{C}(\text{H})(\text{C}_6\text{H}_5)_3\text{N(CH}_3)_2 \xrightarrow{\text{O}} \\
 \text{C}(\text{OH})(\text{C}_6\text{H}_5)_3\text{N(CH}_3)_2 \xrightarrow{\text{H}^+} \text{C}(\text{C}_6\text{H}_5)_3\text{N(CH}_3)_2 + \text{Oxalate}^+
 \end{array}$$

CRYSTAL VIOLET  
(*Hexamethylpararosaniline*)

Dimethylaniline	... 12 g.
Michler's ketone	... 5 g.
Phosphorus oxychloride	... 5 g.

The three substances in quantities indicated above are introduced into a 500 c.c. round bottom flask and heated for about four hours by immersing the flask in a vigorously boiling water-bath. In the course of about half an hour the mixture solidifies to a cake and the heating is continued for the period indicated above. 100 c.c. of water are poured into the flask and the blue solution rendered alkaline with a solution of caustic soda and steam distilled to remove the unchanged dimethylaniline. The flask is cooled, the reddish solid separated by filtration and boiled with a mixture of 250 c.c. of water to which only 2 c.c. of concentrated hydrochloric acid have been added. The blue solution is allowed to settle and filtered through a folded filter-paper. Any residue is treated similarly, using 100 c.c. of the same acid solution till the whole of it goes into solution. The combined filtrate is cooled and treated while stirring well, with finely powdered common salt (50 g.) until the dye is precipitated. The dye is filtered and recrystallised in a 50 c.c. beaker using about 5 to 10 c.c. of water. Crystal Violet separates from the solution in fine crystals having a bronze-like lustre which are dried in air. Yield 8 g.

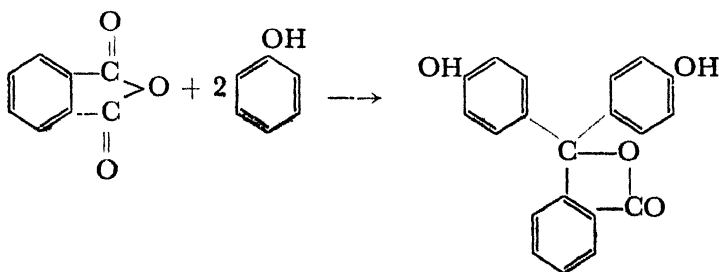


**Preparation 122****PHENOLPHTHALEIN**

Phenol	... 20 g.
Phthalic anhydride	... 10 g.
Concentrated sulphuric acid	... 8 g.

The mixture of phenol, phthalic anhydride and sulphuric acid is heated in a 250 c.c. round-bottom flask fitted with an air-condenser for about 4 hours in an oil bath at 120°. The red oil formed is poured into a 2-litre round-bottom flask containing about 500 c.c. of water. The phenol is removed by steam distillation. The residual liquid is filtered, the precipitate washed with water, dissolved in 10 per cent. caustic soda solution and again filtered. The filtrate is acidified with acetic acid and a few drops of hydrochloric acid and after standing overnight, the precipitate is filtered and dried between folds of filter paper.

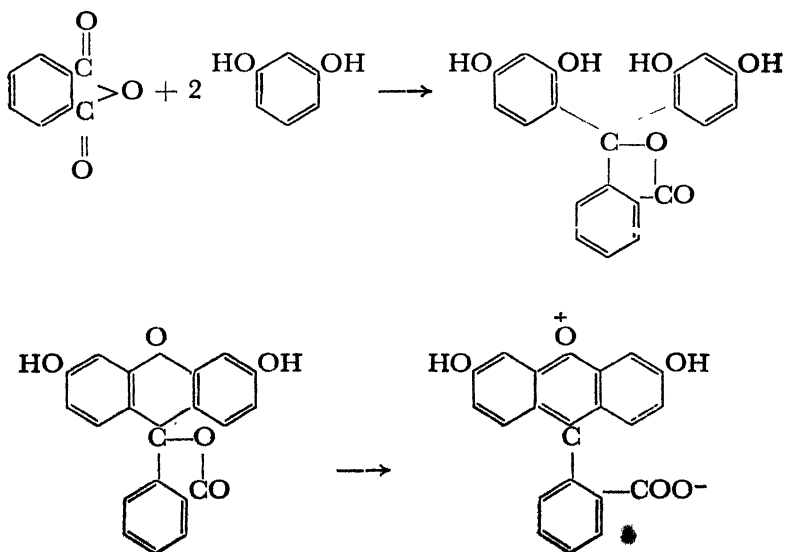
This is purified by boiling with excess of absolute alcohol under reflux (using for every gram of substance 5 c.c. of absolute alcohol, and 0.5 g. of decolourising charcoal). The solution is filtered hot and the residue washed with boiling absolute alcohol. The combined filtrate and washings are distilled to half the bulk, then diluted with 8 volumes of water and filtered through cloth to remove any resinous matter. The filtrate is evaporated on a water-bath till the phenolphthalein crystallises. It is a white granular crystalline powder ; m.p. 250-253°. Yield, 5 to 6 g.



**Preparation 123****FLUORESC EIN**

Phthalic anhydride	...	7.5 g.
Resorcinol	...	11 g.
Anhydrous zinc chloride	...	3.5 g.

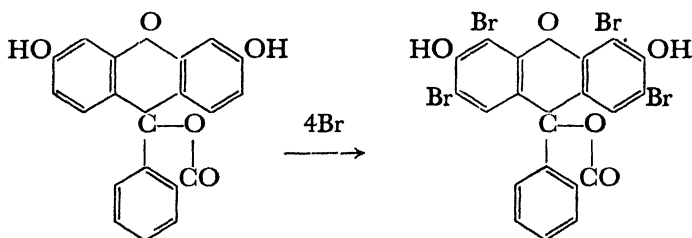
An intimate mixture of 7.5 g. of phthalic anhydride and 11 g. of resorcinol is heated to 180° (internal temperature) in a 500 c.c. round-bottom flask placed in an oil-bath. 3.5 g. of powdered anhydrous zinc chloride are added in small portions during 45 minutes, stirring with the thermometer. At the end, the mass becomes so viscous that stirring is not possible. The oil bath is allowed to cool to 90° and a mixture of 100 c.c. water and 5 c.c. concentrated hydrochloric acid is added to the reaction mixture. The temperature of the oil bath is raised until the water boils. The mixture is stirred, till the reaction mass disintegrates and the zinc salts have dissolved. The mass is filtered, the residue ground with water in a mortar, filtered and dried at 100°. Yield, 15 g. The fluorescein so obtained is purified by dissolving it in sodium hydroxide solution, filtering and acidifying the filtrate when pure fluorescein is precipitated.



**Preparation 124****EOSIN**

Fluorescein	... 8.5 g.
Bromine	... 18 g. (6 c.c.)

8.5 g. of powdered fluorescein and 40 c.c. of rectified spirits are kept in a 250 c.c. round bottom flask and bromine (18 g.) is added dropwise from a separating funnel. When half the bromine has been added, a clear solution results and crystalline material separates out on further addition of bromine. The reaction mixture is allowed to stand for 2 hours and the eosin is filtered and washed with alcohol and dried at 100°. Yiled, 12.5 g.



**Preparation 125****METHYLENE BLUE**

<i>p</i> -Nitrosodimethylaniline HCl	... 18 g.
Concentrated hydrochloric acid	... 60 c.c.
Iron Filings	... 20 g.

**(a) *p*-Aminodimethylaniline**

The *p*-nitrosodimethylaniline hydrochloride as obtained from preparation (45) is dissolved in 100 c.c. water and 60 c.c. of con. hydrochloric acid are added to the solution. Iron filings in 4 g. lots are then added with stirring maintaining the temperature between 20-25° with addition of ice. The reduction is regarded as complete when a drop of the solution placed on a filter paper is practically colourless. The solution, pale brown in colour, is treated with lime paste till faintly acid to congo paper, after which neutralisation is completed by addition of chalk until there is no effervescence. The mixture is filtered and washed.

**(b) Preparation of the dye**

Solution I. 33.5 g. of sodium thiosulphate in 40 c.c. water.

Solution II. 26.4 g. of sodium dichromate in 40 c.c. water.

Solution III. 14.0 g. of dimethylaniline in 21 c.c. of concentrated hydrochloric acid.

Solution IV. Sodium dichromate same as II.

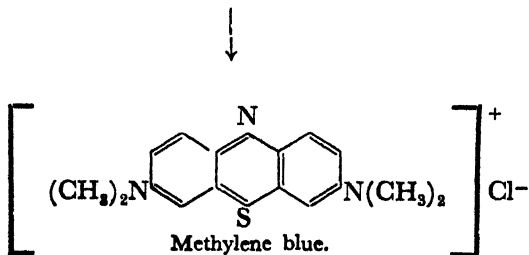
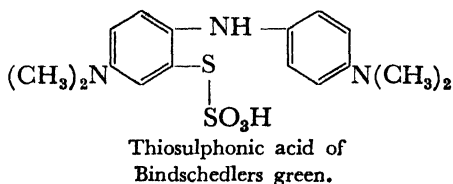
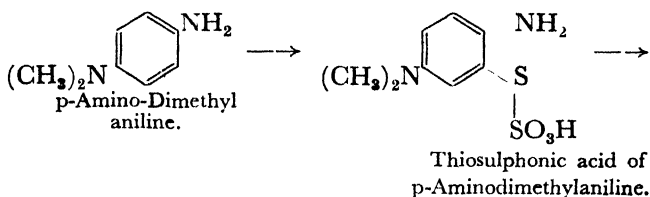
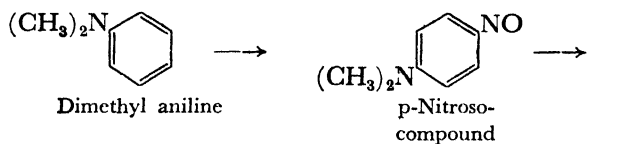
Solution V. 1.5 g. of copper sulphate in 20 c.c. of water.

The clear neutral solution of *p*-aminodimethylaniline, is transferred to a litre beaker and kept stirred by a mechanical stirrer. Solution I is added all at once and then solution II in about two minutes. After a further interval of two minutes solution III is added all at once and immediately following it solution IV in about two minutes. After an interval of about 7 minutes the last solution is added. The mixture is then transferred to a big porcelain basin, heated to boiling and filtered in a large Buchner funnel. The precipitate of chromium hydroxide is washed with boiling water until the filtrate is only faintly coloured.

To prepare the zinc salt, the total filtrate, about a litre, is treated with 150 g. of common salt, 40 g. of 50% zinc chloride

solution and 10 g. of concentrated hydrochloric acid. The zinc salt separates as a coppery powder on cooling and is filtered off and washed with 10% brine and air dried. Yield, 30 g.

If pure methylene blue free from zinc is required, the filtrate is heated to  $80^{\circ}$ , treated with 15 g. of common salt for every 100 c.c. of the solution and only 10 c.c. of concentrated hydrochloric acid. On cooling, the zinc-free methylene blue separates as crystals



**Preparation 126****INDIGO****(a) Phthalic acid**

Naphthalene	... 15 g.
Concentrated sulphuric acid	... 120 c.c.
Mercuric sulphate	... 8 g.

The mixture of naphthalene, sulphuric acid and mercuric sulphate are introduced into a 300 c.c. retort to the tubulure of which an air condenser is luted by asbestos paper and plaster of Paris. The retort is clamped with the neck sloping upwards as a refluxing arrangement and the contents are heated gently over a wire-gauze with occasional shaking until the floating liquid layer of naphthalene dissolves. The retort is now tilted and clamped as for distillation, the end of the condenser dipping into a beaker of water. The contents are heated carefully at first and then strongly. In the neighbourhood of 250° the liquid darkens in colour and oxidation commences with evolution of sulphur dioxide. The distillate that collects consists of some unchanged naphthalene, phthalic acid and anhydride. Care should be taken that the condenser tube is not clogged, by gently heating it all along occasionally. The distillate is filtered, the precipitate well washed with water, dissolved in a small amount of dilute caustic soda, filtered and the acid precipitated with dilute hydrochloric acid. The acid is recrystallised from water or dilute alcohol. It crystallises in plates with no definite melting point. Yield, 8 g. (The operation should be conducted in a fume cup-board.)

**(b) Phthalic anhydride**

10 g. of phthalic acid are sublimed as described on p. 11. Long needles collect on the filter paper. Yield, 8 g.

**(c) Phthalimide**

Phthalic anhydride (resublimed)	... 15 g.
Urea	... 3.5 g.

The two substances are intimately mixed in a mortar and introduced into a 500 c.c. round-bottom flask, with a thermometer dipping in the mixture. The flask is heated at 130-135° in an oil bath. The mass shows a tendency to froth up, the temperature rising at the same time to nearly 160°. When ammonia is no longer evolved, the reaction is over and the spongy solid is stirred up with a little water and filtered. The product is dried in the



air oven and is used for the next preparation. One gram of the substance may be recrystallised from ether ; m.p.  $233^{\circ}$ . Yield, 12 g.

(d) **Anthranilic acid**

Sodium hydroxide	... 20 g. in 100 c.c. water
Phthalimide	... 15 g. <i>( // )</i>
Bromine	... 5 c.c.
Con. hydrochloric acid	... 45 c.c.
Glacial acetic acid	... 15 c.c.
Sodium hydroxide (flakes)	... 20 g.

The sodium hydroxide solution is taken in a wide mouthed 250 c.c. conical flask, and cooled to  $-5^{\circ}$  in a freezing mixture of ice and salt. The bromine is added slowly from a burette with constant stirring. The phthalimide is made into a paste with water and added to the cold hypobromite solution and stirred vigorously, using a mechanical stirrer. After ten minutes, the flask is removed from the freezing mixture and the contents allowed to reach nearly the room temperature. The sodium hydroxide flakes are added next little by little and warmed to  $80^{\circ}$  for a few minutes (5 to 10). The liquid is filtered if necessary, transferred to a 600 c.c. beaker cooled in a mixture of ice and salt and acidified with hydrochloric acid till just neutral and finally the glacial acetic acid is added. After five minutes, the crystals are filtered, washed with a little water, and recrystallised from hot water adding norit. It is preferable to add a few c.c. of sulphurous acid during crystallisation. Anthranilic acid crystallises in needles, m.p.  $143-144^{\circ}$ . Yield, 12 g.

(e) **Phenylglycine o-carboxylic acid.**

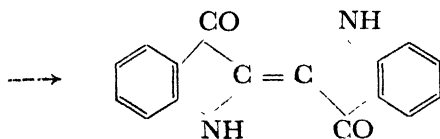
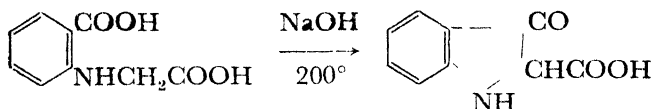
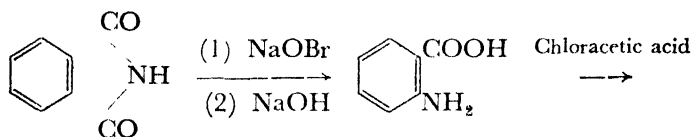
Anthranilic acid	... 13.6 g.
Chloroacetic acid	... 11.4 g.
Sodium carbonate	... 17 g. in 100 c.c. of water <i>10 gms in 60 c.c. water</i>

The mixture is heated in a round-bottom flask on a water bath under reflux at  $60-80^{\circ}$  for about two and a half hours. The reaction mixture is neutralised with hydrochloric acid and after standing the phenylglycine o-carboxylic acid which separates out is filtered and recrystallised from water. A further yield can be obtained by evaporating the filtrate. It consists of colourless crystals, m. p.  $200^{\circ}$ . Yield, 15 g.

**(f) Indigo**

Phenylglycine o-carboxylic acid	... 10 g.
Caustic potash	... 20 g.
Water	... 10 c.c.

The acid is added to a solution of the caustic potash in the requisite amount of water contained in a nickel crucible and the mixture evaporated quickly with constant stirring until quite dry. It is powdered and added to 8 parts of paraffin (m.p.  $20^{\circ}$ ) and the mixture heated in the crucible to  $250-270^{\circ}$  while stirring with a thermometer the bulb of which is enclosed in a closed glass tube and containing some mercury. Steam is evolved and the end of the reaction is indicated by the strong yellow colour of the fusion. The homogenous paste is cooled and boiled with water (200 c.c.) containing a little sodium hydrosulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) to prevent oxidation. The liquid is filtered from the paraffin and oxidised by passing air. For this purpose the solution is placed in a Buchner flask fitted with a one-holed cork carrying a glass tube which dips into the solution and the flask is connected to the pump. Indigo is precipitated as a dark blue powder. It is filtered, washed with water and dried. Yield, 3-4 g.



## Preparation 127

### COPPER PHTHALOCYANINE

#### (a) Phthalamide :

Phthalamide	... 20 g.
Ammonia (0.88 sp.gr.)	... 60 c.c.

20 g. of phthalamide are taken in a 250 c.c. round bottom flask and the ammonia added to it. The mixture is stirred mechanically for 24 hours. It is then filtered, washed with water and dried at 100°. The yield is 20 g. Phthalamide melts with decomposition at 220°.

#### (b) Phthalonitrile :

Phthalamide	... 20 g.
Acetic anhydride	... 75 c.c.

In a 500 c.c. round-bottom flask, provided with a reflux condenser, 20 g. of phthalamide and 75 c.c. of acetic anhydride are placed. The mixture is refluxed for 5 to 6 hours and allowed to cool. While still hot, it is carefully poured into 150 c.c. of boiling water in a beaker to decompose excess acetic anhydride. The beaker is then cooled in ice and the reaction mixture rendered alkaline with sodium hydroxide solution. The precipitated Phthalonitrile is filtered at the pump, washed with water and dried at 100°. The yield of the crude nitrile is 15 g. It is purified by repeated crystallisations from benzene. Pure phthalonitrile melts at 141°. The nitrile is also purified by distillation under reduced pressure and then crystallizing from benzene.

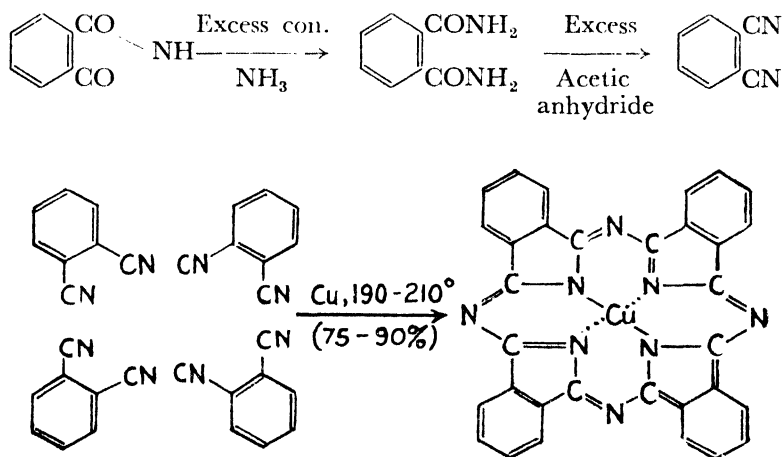
#### (c) Copper Phthalocyanine :

Phthalonitrile	... 12.8 g.
Copper bronze	... 1.6 g.

Phthalonitrile and copper bronze are taken in a 100 c.c. pyrex round bottom bolt-head flask and heated in an oil-bath, the reaction mixture being stirred by a thermometer. The product turns green at 190° and becomes a paste at 220°. The bath temperature is maintained at 220° for 15 minutes. The internal temperature rises rapidly and at times exceeds that of the bath by 40-50° and stirring becomes impossible. The mass is allowed to cool slightly

and then ground with alcohol. It is refluxed with alcohol and filtered hot ; this removes phthalonitrile. The residue is dried at  $100^{\circ}$ . It weighs about 10 g. and contains a little copper bronze.

To free the copper phthalocyanine from copper, it is finely ground and stirred mechanically with 55 c.c. of concentrated sulphuric acid and then allowed to stand for an hour. The solution is then filtered through a sintered glass funnel, washed with concentrated sulphuric acid. The combined filtrate and washings are then poured into 100 g. of finely crushed ice with stirring. The flocculent blue precipitate that appears is allowed to stand for 2 to 3 hours ; and then filtered at the pump and washed with boiling water. The pigment is then refluxed with alcohol, filtered and dried at  $100^{\circ}$ .



## CHAPTER X

### QUANTITATIVE ORGANIC ANALYSIS

#### 1. Melting and freezing points of a binary mixture and construction of a phase diagram

This diagram is usually constructed with a view to investigate whether two substances unite to form an additive compound or form mixed crystals. In the former case, the curve is made up of three branches, the middle branch being between two eutectics. The highest point in the middle branch is the melting or solidifying point of the definite compound the composition of which can be obtained from the curve.

Before attempting the experiment, it is first necessary to fix up the composition of the various mixtures of which the melting points are to be determined. The composition should be adjusted so that at least ten points are introduced in the curve. The following concentration ratio will be convenient :

Component A	0.5	.45	.4	.35	.3	.25	.2	.15	.1	.05	.0
Component B	.0	.05	.1	.15	.2	.25	.3	.35	.4	.45	.5
% A	100	90	80	70	60	50	40	30	20	10	0

**Experiment.** In several corked specimen tubes ( $3'' \times 5/8''$ ) the two components are introduced in quantities as indicated above. They are completely melted in a paraffin or glycerine bath which is maintained at a temperature about  $10^\circ$  higher than the melting point of the mixture and the mixture is stirred with a stout nickel wire (1 mm.). The mixture is cooled and a small amount of it is crushed on a porous plate and the melting point of the mixture is determined as usual. In this way the melting points of the pure components and the various mixtures are obtained. Since the melting points are usually not identical with the solidifying points, the solidifying points for each mixture are also determined and the mean of the melting and solidifying points is taken in each case for the purpose of constructing the curve.

To determine the solidifying points the arrangement is similar to that adopted for the determination of freezing points in molecular weight determinations by Beckmann's method.

Each of the specimen tubes is fitted with a one-holed cork with a slit for the stirrer to pass through. A thermometer with a small bulb is introduced, and the specimen tube fitted by a piece of rubber tubing into another wider tube (6"  $\times$  1"), the latter serving as an air-jacket (Fig. 46). The specimen tube is then detached and fixed to a clamp and the mixture melted by directly immersing in a paraffin-oil bath which is heated by a micro-burner to a temperature of about 10° higher than the melting point of the mixture. The bath liquid adhering outside is wiped off and the molten mixture is allowed to cool slowly with stirring in the air-jacket till crystals appear. The maximum temperature indicated is the solidifying point. The mean of two determinations should be taken as the solidifying point.

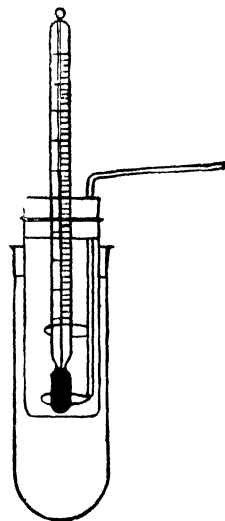


Fig. 46. Apparatus for determination of the freezing point of a mixture of two solids.

The composition of each mixture expressed as percentage by weight is plotted against the average of the melting and solidifying points as shown (Fig. 47). The percentage composition corresponding to the maximum in the middle branch of the curve is the

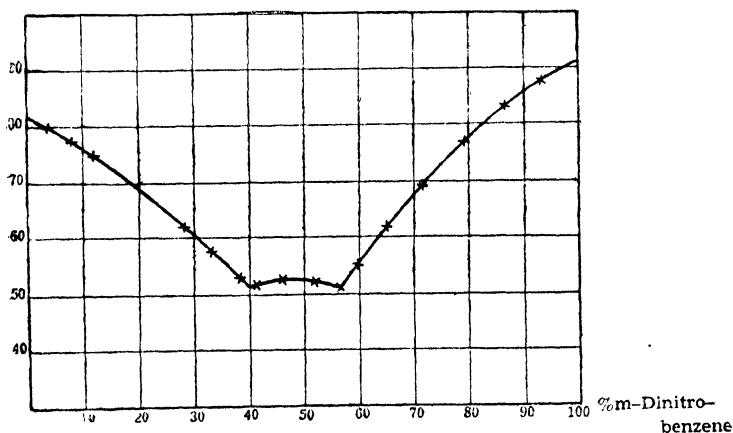


Fig. 47. Phase diagram showing the formation of a compound between two components (Naphthalene and m-dinitrobenzene.)

composition of the addition compound and the temperature indicated is the temperature at which it will melt. In the absence of a maximum between two eutectics the inference is drawn that the components do not form an addition compound.

To determine the molecular proportion in which the two components unite to form the definite compound, the percentage by weight of each component is divided by the molecular weight and the ratio is reduced to the ratio of the nearest integers.

The melting point curves for the following binary mixtures may be studied :—

	Molecular ratio of the com- ponents in the com- pound.	M.P.
(1) m-Dinitrobenzene and Naphthalene	1 : 1	52°
(2) Naphthalene and Picric acid	1 : 1	149°
(3) Resorcinol and Picric acid	1 : 1	100·3
(4) $\alpha$ -Naphthol and p-Toluidine	1 : 1	53·5

## 2. Determination of the Equivalent weight of an acid.

Organic acids are very frequently characterised by determining their equivalents. If the acid is obtainable only in solution or is present as the soluble sodium salt, as in the hydrolysis of an ester, the silver salt is prepared and the equivalent weight determined by the ignition of the silver salt. This method is particularly suitable for the lower aliphatic acids, such as acetic, propionic, butyric etc., all of which are liquids and very soluble in water.

### Equivalent of an acid by titration with standard alkali

N/10 aqueous or alcoholic potash or baryta is used for titrating organic acids with phenolphthalein as indicator. Baryta is mostly preferred for this purpose as it can be prepared and kept free from carbonate. A sharp end point is obtainable only when there is no carbonate present in the alkali solution.

**Preparation of Baryta :** Pure crystalline  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  (Equivalent 158·1) is used. 17 g. of the substance are finely powdered and transferred to a two litre bottle and about a litre of distilled water previously boiled and cooled is added. The bottle is corked, shaken and kept over night. The clear solution is quickly decanted into the storage bottle of the

baryta-burette (Fig. 48) the parts of which are next assembled and the alkali protected by guard tubes containing soda-lime.

**Standardisation.** The baryta is standardised against pure N/10 succinic acid or oxalic acid.

**Determination of equivalent weight.**

If the acid is soluble in water, 1–2 g. are accurately weighed, dissolved in water and the solution made up to 100 c.c. 20 c.c. of the solution are titrated against the standard baryta, of which not less than 10 c.c. should be used during each titration.

If the acid is insoluble in water, 0.2 to 0.3 g. of acid is weighed into a beaker or conical flask, 20 c.c. of rectified spirits added to dissolve the acid and the solution titrated against baryta. A correction may be applied by taking the same volume of the solvent (water or alcohol) and finding the volume of alkali required to produce a pink colour with phenolphthalein.

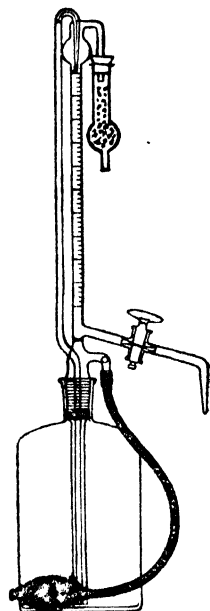


Fig. 48 Baryta burette

$$\text{Equivalent weight} = \frac{W \times 1000}{V} \text{ phenolphthalicn,}$$

where  $W$  = weight of acid taken,

and  $V$  = volume of N-baryta required in c.c.

**Equivalent weight by analysis of silver salts.** Silver salts are the most suitable because they are normal salts, are generally insoluble in water, are easily purified, contain no water of crystallisation and are easily decomposed by heat. They are however highly sensitive to light and should on that account be dried and preserved in a dark place. A few of them, e.g. silver oxalate, explode on heating.

**Preparation of the salt.** (1) About 2 g. of the acid are taken in a beaker, 10–15 c.c. of water are added and dilute ammonia run in drop by drop from a pipette till there is a slight excess. The excess of ammonia is removed by boiling and the cold liquid is tested with litmus to see if it is neutral. Silver nitrate in slight excess (4 g. in 20 c.c. water) is added, the precipitated silver salt



is filtered at the pump, washed with cold water, dried on a porous plate and then in the vacuum desiccator or in the steam oven.

(2) When the ammonium salt is easily hydrolysable (phthalic acid), the acid is neutralised by pure sodium hydroxide free from carbonate and a drop of nitric acid is added to make the liquid slightly acidic. Silver nitrate is added as before and the silver salt filtered washed and dried. Too much washing is to be avoided.

(3) When the acid is present as the sodium salt, say in the hydrolysis of an ester, the liquid is carefully neutralised with dilute nitric acid and evaporated to dryness on a water-bath to drive off all the alcohol. The sodium salt thus obtained is used to prepare the silver salt in the usual way.

**Ignition of the silver salt.** 0.5 to 1 g. of the dry silver salt is weighed out accurately in a tared porcelain crucible and the salt is heated very cautiously at first so as to avoid any of the contents being forced out by the violence of the reaction. When the organic matter has been completely destroyed, the crucible is maintained at a dull red heat for a few minutes and then cooled in a desiccator. The silver is weighed and from the weight of silver the equivalent weight of the acid is calculated.

$$\text{Equivalent weight} = \frac{W \times 108}{x} - 108 + 1,$$

where  $W$  = weight of salt taken,

and  $x$  = weight of silver obtained.

### 3. Determination of the Equivalent weight of a base.

The equivalent weight of a base is usually determined either (a) volumetrically, by preparing a crystalline salt with a mineral or organic acid, purifying the salt and then titrating the amount of acid present in the salt by standard baryta, or (b) gravimetrically, by preparing the chloroplatinate of the base, igniting a known weight of it and weighing the residue of pure platinum.

**Volumetric methods.** The most suitable salts are the hydrochlorides, sulphates, salicylates or 3 : 5-dinitrobenzoates.

**Preparation of the hydrochlorides.** 1-2 g. of the freshly-distilled base are dissolved in 5-10 c.c. of dry benzene and a stream of dry hydrogen chloride is led through a wide tube into the solution of the base. The amount of benzene used should be just sufficient to dissolve the base. After cooling, the hydrochloride that is precipitated is filtered off, washed with dry ether to remove any free base, and dried on a porous plate.

The hydrochlorides of aniline, o- and p- toluidines, phenetidine, anisidine and  $\beta$ -naphthylamine are prepared easily by this method.

**Determination of the equivalent.** 0.5 to 1 g. of the hydrochloride is dissolved or suspended in water and titrated against standard baryta using phenolphthalein as indicator. In general, the amount of the salt used should correspond to about 30 to 50 c.c. standard alkali. The equivalent weight of the base is calculated thus :

Let  $W$  be the weight of the hydrochloride taken and  $V$  c.c. of the baryta be required (expressed as normal alkali).

Then the equivalent  $E_1$  of the hydrochloride  $= \frac{W}{V} \times 1000$   
where  $V = \text{titre value} \times \text{normality factor}$ .

Then the equivalent of the base is  $E_1 - 36.5$ .

(At least two determinations should be carried out.)

**Preparation of the salicylate.** 1 gram of the base and an amount of the acid slightly less than that theoretically required (roughly 1 g.) are dissolved in dry benzene and refluxed for about 20 minutes. The mixture is cooled and ligroin added little by little till precipitation of the salicylate is complete. The salicylate is filtered, and recrystallised by solution in benzene and reprecipitated with ligroin. It is then dried by pressing on a porous plate.

0.5 to 1 g. is dissolved in 20 c.c. of rectified spirits and titrated against baryta. A blank is carried out with the same volume of alcohol. The calculation is exactly as described above.

Equivalent of base  $= E_1 - 138$ .

The salicylates of o- and p- toluidine, phenetidine and  $\beta$ -naphthylamine can be prepared by the above method and their equivalents determined.

M.P. of p-toluidine salicylate ...  $64^\circ$

M.P. of o-toluidine salicylate ...  $89^\circ$

**Preparation of 3 : 5-dinitrobenzoates.** 0.01 g. molecule each of the base and the acid are separately dissolved in 10 to 15 c.c. of absolute alcohol, mixed and refluxed for about ten minutes. The solution is poured on watch a glass to crystallise. The salt is purified by recrystallisation from absolute

alcohol. The equivalent of the salt is determined as usual, being  $E_1 - 212$  (molecular weight of the acid).

(Use aniline, 1 c.c., and 3 : 5-dinitrobenzoic acid, 2 g.)

#### 4. Molecular weights of tertiary bases

The method consists in preparing the quaternary ammonium iodide, dissolving it in water after purification, and determining the iodine volumetrically with standard silver nitrate or by Volhard's method. The ease of formation of quaternary ammonium salts is dependent on the constitution of the reactants.

##### Preparation of trimethyl phenyl ammonium iodide.

If the amine and the methyl iodide are perfectly dry the preparation comes out very easily. 2 c.c. of dimethylaniline, freshly distilled and dried over sodium hydroxide, and 1 c.c. of methyl iodide dried over anhydrous calcium chloride are mixed in a corked test tube. Even without warming, the mixture solidifies gradually. The solid is dissolved in the minimum amount of absolute alcohol and the salt precipitated by adding ether (dried over sodium). The precipitate which is practically colourless is filtered, dried on a porous plate and left in a vacuum desiccator.

**Determination of molecular weight.** 0.4 to 0.5 g. of the substance is dissolved in about 20 c.c. of water and the clear solution is titrated against standard N/10 silver nitrate, the end point being determined by the clear point method.

Or, 0.5 g. of the substance after solution in water is treated with excess of standard silver nitrate (N/10) which is added gradually with frequent shaking to coagulate the iodide, till a considerable excess is present. The excess of silver nitrate is titrated against standard ammonium thiocyanate using ferric alum as indicator.

Weight of substance taken =  $w$  g.

Volume of thiocyanate equivalent to 20 c.c. of  
silver nitrate =  $x$  c.c.

Volume of the silver nitrate added =  $y$  c.c.

Volume of thiocyanate required for excess of  
silver nitrate =  $z$  c.c.

Molecular weight of the compound (M)

$$= \frac{w \times 1000}{\left(\frac{x}{20} - z\right)S}$$

where S = strength of thiocyanate expressed as normal.

$\therefore$  the molecular weight of the base  $= M - 142$  ( $\text{CH}_3\text{I}$ ). The molecular weights of the pyridine and quinoline bases can be determined in a similar manner.

**Determination of the equivalent weight by analysis of the platinichloride.** The base is dissolved in a slight excess of 1 : 1 hydrochloric acid and a 10% solution of chloroplatinic acid is added. The precipitate is filtered, washed first with a very small amount of water, then with alcohol and finally dried in the steam oven.

0.2 to 0.3 g. of the salt is ignited just like the silver salt of an organic acid and the residue of metallic platinum weighed.

If  $B$  be the equivalent weight of the base, then the molecular weight of the salt can be calculated from the formula,  $B_2\text{H}_2\text{PtCl}_6$ . One gram molecule of the salt leaves behind 1 gram atom of platinum.

$$\frac{\text{Mol. wt. of the double salt.}}{\text{Atomic wt. of platinum}} = \frac{\text{Weight of salt taken}}{\text{Weight of platinum obtained}}$$

$$(i.e.) \frac{2E + \text{H}_2\text{PtCl}_6}{\text{Pt}} = \frac{W}{W_1}$$

$$2E + 2.016 + \frac{195 + 212.76}{195} = \frac{W}{W_1}$$

$$2E + 409.8 = 195 \times \frac{W}{W_1}$$

$$2E = 195 \times \frac{W}{W_1} - 409.8$$

$$E = \frac{195 \times \frac{W}{W_1} - 409.8}{2}$$

If the acidity of the base is  $n$ , then the molecular weight of the base  $M = n \times E$ .

**Special methods.** Complex tertiary bases often give well-crystallised dichromates of definite composition. The chromic acid in these can be estimated volumetrically by adding an excess of a standard solution of ferrous ammonium sulphate and then titrating the excess with standard permanganate or standard dichromate. Diphenylamine indicator can be used when employing dichromate. The method is useful in the case of quinoline derivatives and with pyridinium and quinolinium salts.

**Equivalent weight of quinoline.** ( $C_9H_7N$ ). The dichromate has the formula  $(C_9H_7N)_2 H_2Cr_2O_7$ , m.p.  $165^\circ$ . 1 c.c. of freshly-distilled quinoline is dissolved in a slight excess of dilute sulphuric acid and a strong solution of potassium dichromate (2.5 g.) is added. The mixture is shaken well, when a copious precipitate of the dichromate is obtained. The precipitate is filtered, washed with cold water and recrystallised from boiling water. The orange-yellow crystals are filtered and dried in a vacuum desiccator.

0.1 to .2 g. of the dried crystals are dissolved in about 50 c.c. of hot water, the solution is cooled and 40 c.c. of ferrous ammonium sulphate are then added with sufficient dilute sulphuric acid. The solution becomes green due to formation of chromic sulphate; the excess of ferrous sulphate is titrated against standard permanganate after diluting to about 200 c.c.

When standard dichromate is employed for determining the excess of ferrous sulphate, 30 c.c. of dilute sulphuric acid, 15 c.c. of phosphoric acid mixture and three drops of the diphenylamine indicator are added, the addition of dichromate being continued till a permanent blue-violet colour is obtained which deepens no further on keeping for a short time.

**Calculation.** 20 c.c. of  $FeSO_4 = x$  c.c. of dichromate or permanganate of strength  $S$  expressed as normal.

Amount of  $FeSO_4$  taken =  $V$  c.c.

Weight of the quinoline dichromate taken =  $m$  g.

Amount of dichromate or permanganate required for excess of ferrous sulphate =  $y$  c.c.

$$\text{Amount used} = \left( \frac{V}{20} x - y \right) S$$

$$\text{Molecular weight of the dichromate} = \frac{m \times 6000}{\left( \frac{V}{20} x - y \right) S}$$

$$E = \frac{\text{Molecular weight of dichromate} - 218}{2}$$

where  $E$  is the equivalent weight of the base.

**Gravimetric method.** A known weight of the quinoline dichromate is taken in a weighed crucible, a little naphthalene is added and the crucible heated cautiously to redness till nothing but chromic oxide is left behind. The weight of the dichromate

leaving behind one gram molecule of chromic oxide, i.e. 152 g., is the molecular weight of the dichromate from which the equivalent is obtained as described above.

### 5. Determination of the Equivalent of an ester

The equivalent weight of an ester may be defined as the weight of the ester required for completely reacting with 1 litre of N alkali. In practice, alcoholic potash is used for the hydrolysis of the ester.

**Preparation of alcoholic potash.** Alcoholic potash of approximately N/2 strength is prepared by dissolving 15 g. of caustic potash pellets in an equal weight of water and diluting to 500 c.c. by addition of absolute alcohol. The solution is agitated with 10-15 g. of anhydrous sodium sulphate until it clarifies, after which the clear solution is decanted. There is no necessity for accurately determining the strength of this solution.

**Estimation.** The ester should always be purified by distillation. 0.5 to 1 g. of the ester are weighed, using a Lunge-Rey pipette, into a 250 c.c. round-bottom flask made of hard resistance or pyrex glass. 30 c.c. of alcoholic potash are added, and the flask is fitted with a reflux condenser. The mixture is boiled gently on a water bath or on a wire-gauze for  $1\frac{1}{2}$  to 2 hours. After cooling, the condenser is washed by running a little water down the inner tube and the excess of potash titrated with N/4 hydrochloric acid using phenolphthalein as indicator.

In order to eliminate errors such as those due to absorption of atmospheric carbon dioxide and the solvent action of alkali on glass itself, a blank is run under identical conditions, using a flask of the same make and capacity and the same volume of alkali but without the ester. The acid required to neutralise the alkali is determined in the same way. If  $V_1$  and  $V_2$  are the volumes required of acid expressed as normal in the two cases, and  $W$  be the weight of the ester taken, then the equivalent weight of the ester

$$E = \frac{W \times 1000}{V_2 - V_1}.$$

For the determination of equivalent weight the following esters may be used: ethyl succinate, ethyl propionate, ethyl acetate, propyl butyrate, methyl benzoate, diethyl phthalate, etc.

## 6. Estimation of an acid and an ester in a mixture of the two

**Determination of the free acid.** 1–2 g. of the mixture are weighed into a conical flask with the help of a Lunge-Rey pipette, sufficient acid-free alcohol is added to dissolve it, and the free acid titrated against standard baryta using phenolphthalein as indicator. The end point is usually sharp unless the ester is easily hydrolysable.

Let  $x$  c.c. of normal baryta be required to react with the free acid in 1 g. of the mixture.

**Determination of the acid and ester.** A similar quantity of the mixture is weighed into a 250 c.c. round-bottom flask and the experiment carried out as described in the previous exercise, using 50 c.c. of alcoholic potash. Let the volume of  $N$  alkali required for both the free acid and ester present in 1 g. of the mixture be  $y$ . Then the amount of alkali required for the ester is  $y - x$ .

If  $E_1$  and  $E_2$  are the equivalents of the acid and ester in the mixture, then

$$\text{the percentage of free acid} = \frac{x \times E_1}{1000} \times 100$$

$$\therefore \text{ester} = \frac{(y - x) E_2 \times 100}{1000}$$

On account of the limited solubility of acids in the esters, mixtures can be made by solution of the two in indifferent solvents, *e.g.*, benzene or toluene or even in alcohol. The following mixtures can be analysed: Ethyl acetate and acetic acid, ethyl cinnamate and cinnamic acid dissolved in benzene or ethyl benzoate and benzoic acid dissolved in alcohol.

## 7. Determination of the Saponification value of an oil

The determination of this constant involves an application of the method of quantitative hydrolysis of esters. Technically, the "saponification value" is the number of milligrams of potassium hydroxide required to hydrolyse 1 gram of the oil or fat. For scientific purposes it is more appropriate to calculate the weight in grams of oil hydrolysed by one gram equivalent of caustic potash (56.1 g). The latter is called the "saponification equivalent."

**Experiment.** 1-2 g. of the oil are weighed into a round-bottom flask, fitted with an air condenser having preferably a ground glass joint, 25 c.c. of N/2 alcoholic potash are added and the flask is heated on a water-bath. The reaction is generally complete in about half an hour and the liquid becomes quite clear. A blank is run simultaneously with the same quantity of alcoholic potash. Both the flasks are cooled and the alkali in both titrated against N/2 HCl using phenolphthalein (1 c.c. of 1% alcoholic solution) as indicator. From the difference in titre values the saponification value is calculated.

Let  $V_1$  c.c. of acid expressed as normal be required in the first case and  $V_2$  in the blank. Then the alkali used up =  $(V_2 - V_1)$  c.c.

1 c.c. of N alkali = 56.1 m.g. of KOH

Hence saponification value =  $\frac{56.1 \times (V_2 - V_1)}{W}$ , where  
W is the weight of oil taken.

The saponification value of the following oils may be determined :—cocoanut oil, castor oil, olive oil, gingely oil and groundnut oil.

## 8. Determination of the Iodine value of an oil

**Definition.** Iodine value is usually expressed as the number of parts by weight of iodine absorbed by 100 parts by weight of an oil or fat.

The determination of the iodine value is of great help in characterising an oil and also in finding the proportion of an adulterant in a sample of the oil. The drying power of an oil is generally proportional to its iodine value. Linseed oil which is a drying oil has a high iodine value while the non-drying cocoanut oil has a very low iodine value.

The following solutions are required for carrying out the determination :—

(1) **Iodine monochloride. (Wijs' solution)** 6.5 g. of pure finely powdered iodine are accurately weighed and dissolved in 500 c.c. of pure glacial acetic acid (melted crystals) contained in a litre round-bottom flask by warming on a water-bath. After the



iodine has dissolved, 50 c.c. of the solution are transferred when cold into another flask and pure dry chlorine is passed in till the colour changes from dark brown to a clear orange tint. The remaining iodine solution is now added, the colour of the solution becoming light brown. The excess of iodine prevents the formation of iodine trichloride. The solution is next heated on a water-bath for twenty minutes. This treatment makes the solution much more stable and the solution maintains its strength over long periods when preserved in a stoppered bottle in the dark. In its interaction, the molecule of iodine chloride is equivalent to one molecule of iodine [ $\text{I Cl} \equiv \text{I}_2$ ].

(2) Standard thiosulphate solution (N/10) prepared as usual and standardised against pure dichromate.

(3) Starch solution. 1 g. of soluble starch in 100 c.c. of boiling water, prepared freshly.

(4) Carbon tetrachloride, dried over calcium chloride and distilled.

(5) Potassium iodide solution (10%).

(6) Sample. The oil, if it is not clear, should be warmed till clear and filtered. Fats and waxes should be melted and filtered using a hot-water funnel.

**Procedure.** In the case of a drying oil, 0.2 g. is weighed from a Lunge-Rey pipette into a clean, dry stoppered bottle of 500 c.c. capacity. If it is a fat of low iodine value (cocoanut oil), 1 to 1.5 g. may be weighed into a small specimen tube which is then slipped into the bottle. The oil or fat is dissolved in 10 c.c. of carbon tetrachloride and 25 c.c. of the iodine monochloride are run in from a pipette noting the time for complete draining. The resulting mixture, if turbid, is cleared by adding more carbon tetrachloride. The stopper is moistened with a few drops of potassium iodide solution and inserted into the bottle which is gently rotated to mix the contents thoroughly. The bottle is kept aside for about half an hour or more after which 20 c.c. of potassium iodide solution are added and then 200 c.c. of water. The mixture is titrated with standard thiosulphate solution using starch as indicator.

A blank determination is carried out without the oil, using exactly the same quantity of carbon tetrachloride and the same pipette for delivering the Wijs' solution.

If B c.c. of thiosulphate are required for the blank and A c.c.

for the excess of iodine monochloride in the actual experiment,

then the iodine value = 
$$\frac{(B - A) \times 0.012692 \times 100 \times S}{W}$$

where S = strength of thiosulphate and W = weight of oil taken.

**Iodine value by Hanus Method.** The reagent used is iodine monobromide and is prepared by dissolving 13.2 g. of pure iodine in 1 litre of glacial acetic acid and adding 3 c.c. of liquid bromine. This solution is quite stable. The time of reaction is 40 minutes and the rest of the procedure is the same as in Wijs' method.

## 9. Refractive Index

Measurements of refractive index are often made for checking the purity of oil samples and sometimes for estimating adulterants. The iodine value of an oil and the refractive index appear to be closely related.

Refractive index measurements can be made rapidly by means of refractometers. Of the various types available, the Abbe refractometer (Fig. 49) possesses several advantages. It gives the refractive index directly for the D line ( $n_D$ ) with an accuracy of 0.0001. Only a few drops of the liquid are necessary and either monochromatic or white light, natural or artificial, may be used. The range of the instrument is from 1.3000 to 1.7000.

**Description of the instrument.** The instrument comprises principally of (1) the prism system ; (2) the telescope, with crosswires in the eye-piece and the compensator for achromatisation of the field ; (3) the sector with the graduated

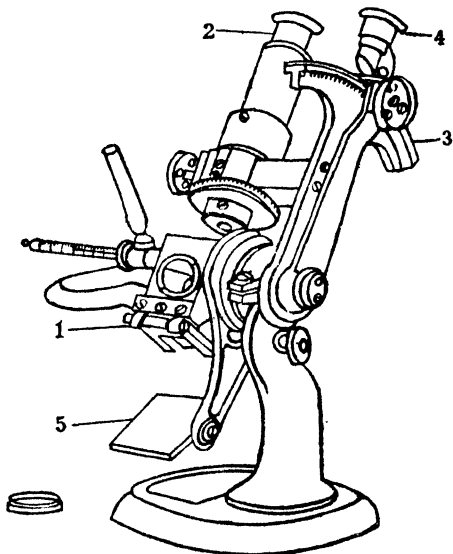


Fig. 49. Abbe Refractometer.

scale ; (4) the reading lens ; and (5) the mirror for reflecting light into the prism system.

The prism system consists of two right-angled prisms of dense flint glass mounted in water jackets which can be clamped together by turning the milled head. In this position the hypotenuses of the two prisms are coincident. The face of the upper prism in contact with the substance investigated is polished while the corresponding face of the lower has a ground surface to prevent the formation of false images. The function of this prism is to introduce light into the liquid. The prisms are so mounted that there is a uniform thin film of liquid between them when the jackets are clamped together. A thermometer mounted in a metal protective cover can be screwed into the water jacket in such a way that the temperature of the outlet water can be read.

The prism system along with the reading lens and the index for reading refractive indices is capable of independent rotation, while the telescope which is rigidly attached to the sector with the engraved scale, is capable of rotation with the prism system between two stops.

To carry out a determination, the prism box is opened, the prism surface is cleaned with a few drops of ether-alcohol mixture or chloroform applied by a cotton wad and wiped dry with a soft cotton cloth. A drop or two of the liquid is placed on the ground surface of the lower prism. The prism box is closed and a film of liquid is thus enclosed between the two prisms. The cross-wires of the telescope are focussed and the mirror adjusted so as to give a good illumination. For this purpose the instrument is placed on a raised table in front of a window. The prism box is turned slowly backwards and forwards until the field of view becomes partly dark and partly illuminated. When ordinary daylight is used the edge of the lighted part shows a coloured fringe which disappears on rotating the compensator by means of the milled screw on the telescope. The prism system is now rotated until the sharp edge coincides with the intersection of the cross-wires in the telescope. The refractive index is read directly by means of the reading lens. The reading has to be taken nearly ten minutes after the introduction of the oil drop.

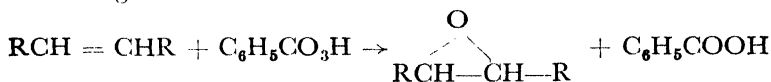
The instrument has to be checked with the glass test piece provided, according to the directions given in the booklet supplied by the makers.

## Refractive Indices, Saponification and Iodine values of some Common Oils.

Name of Oil	Saponification Value	Iodine Value	Index, $n_D^{25^\circ}$ Refractive
Cocoanut	253-262	6-10	1.4530
Castor	175-183	84	1.4771
Olive	185-196	79-88	1.4511 (40°)
Gingelly (Sesame)	188-193	103-117	1.4704-17
Groundnut	186-194	83-100	1.4545 (60°)
Linseed	188-195	175-202	1.4797-1.4802
Cottonseed	194-196	103-111	1.4743-1.4752 (15°)
Mustard (Black)	174	105-110	
			$\frac{\Delta n_D}{\Delta t} = - .0037$

**10. Estimation of unsaturation by Perbenzoic acid titration**

Unsaturated compounds react with perbenzoic acid forming epoxy derivatives. By using an excess of perbenzoic acid and allowing the reaction to proceed at 0-10° for 24 to 48 hours the reaction proceeds practically to completion. The excess of perbenzoic acid is determined iodimetrically and furnishes a measure of the degree of unsaturation.



The method has been found useful in cases where the determination of iodine numbers are unreliable. The reagent is not sensitive to traces of poisons and is therefore useful also when determination of unsaturation by catalytic hydrogenation cannot be employed.

**Preparation of perbenzoic acid reagent.** A solution of 5.2 g. of sodium in 100 c.c. of absolute methyl alcohol is cooled to -5° in a freezing mixture. A solution of 50 g. of commercial benzoyl peroxide in 200 c.c. of chloroform is cooled to 0° and is added without delay to the sodium methylate solution at such a

rate that the temperature does not rise above  $0^{\circ}$ . The mixture is kept in the ice-salt bath with continuous shaking for five minutes, transferred to a 1 litre separatory funnel and the sodium benzoate extracted with 500 c.c. of water containing crushed ice. The chloroform layer is then separated and the aqueous layer is extracted with two 100 c.c. portions of cold chloroform to remove the methyl benzoate. The aqueous solution contains the sodium salt of perbenzoic acid. The perbenzoic acid is liberated by the addition of 225 c.c. of cold 1 N sulphuric acid and is removed from solution by extracting thrice with three 100 c.c. portions of chloroform. The united chloroform solutions are washed twice with 50 c.c. portions of water. The chloroform solution is then dried for an hour over anhydrous sodium sulphate, and the latter removed by filtration. An aliquot portion is added to 50 c.c. of a 5% solution of potassium iodide to which 5 c.c. of glacial acetic acid have been added. The iodine liberated is titrated with a standard solution of 0.1 N sodium thiosulphate solution. The strength of the solution is calculated (the whole solution may contain about 24 g. of perbenzoic acid) and it is diluted with dry chloroform until it is between 0.25 to 0.30 normal.

**Procedure.** A sample of the compound (about 0.5 g.) is weighed out into a glass-stoppered conical flask and is treated with exactly 50 c.c. of the reagent. A blank is run at the same time. Both flasks are placed in a refrigerator for 24 hours. At the end of this time 20 c.c. of 5% solution of potassium iodide, 3 c.c. of glacial acetic acid and 25 c.c. of water are added and the iodine liberated titrated with 0.1 N sodium thiosulphate solution. Starch solution is added just before reaching the end point. The mixture must be shaken vigorously at the end to ensure that the iodine is extracted from the chloroform layer. The difference between the blank and the solution containing the sample represents the amount of perbenzoic acid taken up by the compound. Each ethylenic linkage reacts with one mole of perbenzoic acid.

(Fuller details for the preparation of the perbenzoic acid reagent may be obtained by reference to 'Organic Syntheses', **13**, 86.)

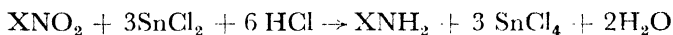
## 11. Estimation of the nitro-group

(a) **Principle of the method.** The estimation is based on the reduction of the nitro-bodies to amino compounds when

treated with an excess of a reducing agent. The excess of the reducing agent is estimated afterwards. Stannous chloride is used ordinarily as the reducing agent.

**Preparation of stannous chloride solution.** 25 g. of tin, either as pure powder or as feathery tin obtained by pouring molten granulated tin into a clean sand-tray, are introduced into a round-bottom flask of 500 c.c. capacity fitted with an air condenser. 250 c.c. of concentrated hydrochloric acid are added and the flask is heated till the reaction commences. Solution of the tin may be hastened by dipping a clean platinum wire into the liquid. When all the tin has dissolved the clear solution is decanted from undissolved matter and made up to a litre.

**Procedure.** 0.2 to 0.4 g. of the non-volatile nitro compound is introduced into a bolt-head flask of 250 c.c. capacity, 30 c.c. of alcohol are added and the flask gently warmed to dissolve the compound. The flask is fitted with a two-holed cork, carrying a leading-in tube for passage of carbon dioxide and a reflux condenser. The air in the flask is displaced by carbon dioxide and a known volume of stannous chloride (50 to 75 c.c.) is added after removing the cork. The cork with the condenser and the leading-in tube is quickly replaced and the flask is heated over a wire gauze for about two hours or longer while a stream of carbon dioxide is bubbling through. While the reduction is going on, the strength of the original stannous chloride is determined by titration with standard iodine using starch as indicator in a flask through which a current of carbon dioxide is passing to prevent atmospheric oxidation. The excess of stannous chloride is determined by titration with standard iodine in the same manner.



$\therefore -\text{NO}_2 = 3\text{SnCl}_2 - 6$  litres of normal solution, since  $\text{SnCl}_2 \equiv \text{I}_2 \equiv 2$  litres of normal solution.

Let the vol. of  $\text{SnCl}_2$  taken

$= V$  c.c. of exactly normal iodine.

Let excess of  $\text{SnCl}_2 = V_1$  c.c. of exactly normal iodine.

$\therefore \text{SnCl}_2$  used up  $= V - V_1$  (normal iodine).

$$\% \text{NO}_2 = \frac{(V - V_1) \times 46 \times 100}{6000 \times m},$$

where  $m$  = weight of nitro body taken.

From the percentage of the nitro group the weight of the substance which contains one nitro group (46 g. of it) can be calculated. Then the number of nitro groups present

$$= \frac{\text{Molecular weight}}{\text{Weight of substance which contains one nitro group}}$$

The following compounds may be used for estimating the nitro group :--

- (1) *m*-Dinitrobenzene.
- (2) *p*-Nitrotoluene.
- (3) *p*-Nitrochlorobenzene.
- (4) Nitrobenzene.
- (5) *o*-Nitrotoluene.

In the estimation of the nitro group, titanous chloride is also frequently employed as a reducing agent, the time taken for reduction being considerably less. The chief precaution to be taken is to store the standard titanous chloride in an inert atmosphere of  $\text{CO}_2$  or  $\text{H}_2$ .

**Preparation of titanous chloride solution.** 50 c.c. of

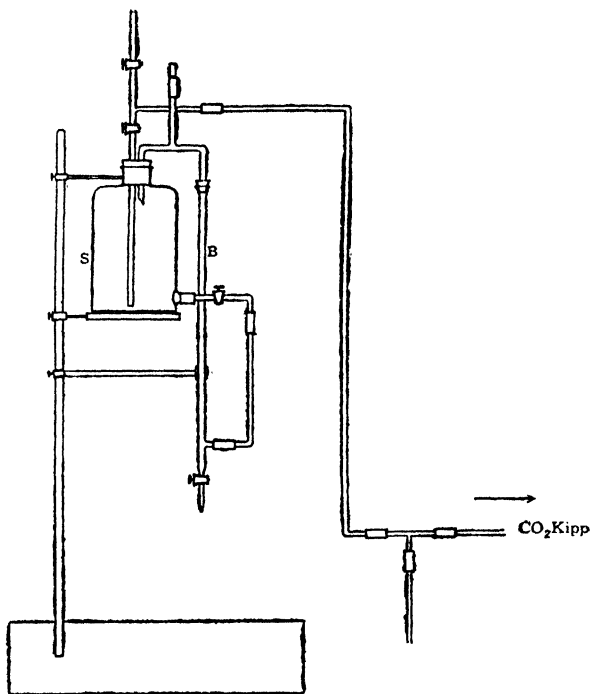


Fig. 50.

commercial titanous chloride solution (20%) are boiled with 100 c.c. of concentrated hydrochloric acid. This solution is diluted to a litre in the storage bottle and treated with 10 g. of pure zinc to reduce any titanous salt present. After the zinc has dissolved the solution is made up to 2 litres with air-free distilled water in the storage bottle connected to a burette (Fig. 90). The space above the solution should be filled with  $\text{CO}_2$  or hydrogen from a Kipp.

**Titanous sulphate.** In the presence of 2N sulphuric acid, titanous sulphate is fairly stable. Hence no special apparatus is necessary.

**Preparation.** Fifty c.c. of 15% solution are measured into a flask containing 100 c.c. of dilute sulphuric acid (1 acid : 3 water), the mixture boiled in a current of carbon dioxide, rapidly cooled under the tap and made up to 2 litres and preserved in a bottle closed with a tight fitting stopper.

**Precaution.** In an open vessel the strength changes appreciably but in the burette it remains constant for 2-3 hours. Each time the burette is to be filled from the stock bottle. The solution should be standardised each time before use.

**Indicator.** 5% potassium or ammonium thiocyanate.

**Standardisation of titanous chloride or sulphate.** To standardise the solution, pure ferrous ammonium sulphate (3.5 g.) is dissolved in dilute sulphuric acid and made up to 250 c.c. by adding air-free water and dilute sulphuric acid alternately. 25 c.c. of this solution are oxidised by running in  $\text{N}/50 \text{KMnO}_4$  carefully from a burette till a faint pink colour is produced. 10 c.c. of a strong solution of potassium or ammonium thiocyanate are added and the titanous chloride run in till the deep red colour disappears.

A standard ferric alum solution (14 g. per litre) acidified with sulphuric acid till the solution is clear, is standardised accurately against the standard titanous chloride and used for periodical standardisation of the titanous chloride whose strength slowly diminishes on keeping.

**Estimation of the nitro group.** About 0.1 to 0.2 g. of the nitro compound is dissolved in sufficient water, dilute hydrochloric acid or alcohol which ever dissolves it, in a 250 c.c. conical flask, the air in it is displaced by  $\text{CO}_2$  and an excess of titanous chloride solution (50 c.c.) added. The mixture is boiled while a



current of  $\text{CO}_2$  is passing through, for 15-20 minutes, cooled and the excess of titanous chloride is titrated with standard ferric alum, using 10 c.c. of the thiocyanate solution as indicator. When the nitro compound is insoluble in any of the above-mentioned solvents, it is sulphonated by heating on the water-bath with 20 c.c. of fuming sulphuric acid for about two hours and then treated with titanous chloride, the rest of the procedure being the same. A blank must be run when alcohol is used as a solvent.

### Calculation

Let  $x$  be the volume of the titanous chloride added,  $y$  the volume of remaining in excess and  $z$  the volume taken up in the blank (when performed) for  $w$  g. of the nitro-compound.

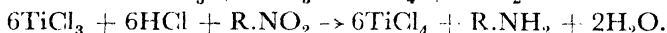
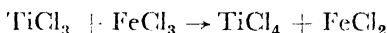
Then the volume required for reducing the nitro-compound is  $x - y - z$ .

Then the weight of the compound containing 1 nitro-group

$$= \frac{w \times 6000}{(x - y - z)N} = n \text{ (say),}$$

where  $N$  is the normality of the solution.

If  $M$  be the molecular weight of the compound, then the number of nitro groups present  $= M/n$ .



$\therefore 6\text{TiCl}_3 \equiv -\text{NO}_2$ , i.e., 1  $\text{NO}_2$  group is equivalent to 6 litres of normal titanous chloride solution.

## 12. Estimation of Amines

**Diazotisation methods.** Primary aromatic amines are usually estimated :

(1) by direct titration in acid solution with standard sodium nitrite ;

(2) by first diazotising with nitrite solution as in (1) and subsequent coupling with an alkaline solution of R-salt of known strength.

### Standard solutions

**Sodium nitrite ( $N/2$ ).** 35 g. of pure sodium nitrite (A.R) are dissolved in water, made up to a litre and stored in a baryta burette, (Fig. 48). This solution is standardised against permanganate as usual. Pure recrystallised sulphanilic acid

dried at  $120^{\circ}$  is used for standardisation when the nitrite used is not very pure. 43.25 g. of the acid are dissolved in 25 c.c. of pure (20%) ammonia, the solution diluted to 500 c.c. and kept in a coloured bottle. 25 c.c. of the N/2 sulphanilic acid are measured into a 400 c.c. beaker, 8-10 c.c. of concentrated hydrochloric acid added and then about 100 g. of washed ice. The nitrite solution is run down the sides of the beaker which is held obliquely, till about 20 c.c. have been added. The contents of the beaker are stirred with a glass rod and the addition of the nitrite continued till a drop of the liquid confers an immediate blue colour on starch iodide paper. The test is again applied after an interval of five minutes to see if there is an excess of nitrite. Otherwise more nitrite is added till the test is answered. The strength of the nitrite solution is adjusted to N/2 by addition of the calculated amount of water.

**Aniline (N/2).** Aniline is purified by distillation, the fraction coming over within half a degree of the correct boiling point being collected. Exactly 23.25 g. of aniline are weighed into a 250 c.c. beaker, 50 c.c. of ice-water added, the beaker cooled in ice, and 38 c.c. of concentrated hydrochloric acid are run in drops with stirring to avoid escape of fumes. The solution is diluted to 500 c.c. and used without standardisation.

**Diazonium solution (N/20).** Exactly 50 c.c. of N/2 aniline solution are taken in a 500 c.c. flask, 10 c.c. of concentrated hydrochloric acid are added and the mixture cooled to  $0^{\circ}$  in ice water. 50 c.c. of nitrite solution (N/2) are run in from the burette and the flask kept gently rotated during the addition. After keeping for about twenty minutes, the solution is diluted to 500 c.c. and kept cold by cooling in ice water in the dark for a few hours.

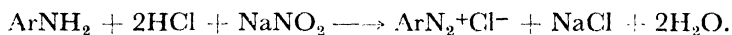
**R Salt (N/20).** 10 g. of the commercial "R Salt" are dissolved in water and made up to 500 c.c. It is standardised thus: 50 c.c. of the diazonium solution (N/20) are transferred to a measuring cylinder cooled in ice. 25 c.c. of the R salt solution are taken in a beaker, 4 g. of sodium carbonate are added and the mixture stirred till a clear solution is obtained. 15 c.c. of the diazonium solution are added from the measuring cylinder. The red dye formed is precipitated by adding sodium chloride. A drop of the solution with the dye suspended is placed on filter paper (used for spot tests). The unreacted solution

spreads out round the deposit of dye and is tested by touching with a glass rod dipped in the diazonium solution other than that contained in the measuring cylinder. Formation of a red dye indicates that an insufficient amount of the diazonium solution has been added. More of the diazonium solution is added from a graduated pipette till a drop tested as before on spot paper no longer forms a dye. When it is difficult to salt out the dye owing to its high solubility, small heaps of common salt are placed on the spot paper, a drop of the solution is placed at a time on a single heap whereby the dye gets precipitated, and the out-spread is tested as before with the diazonium solution. The experiment is repeated adding all but 1 c.c. of the diazonium solution and the titration completed as before.

Since 1 molecule of the R salt couples with 1 molecule of the diazonium compound, the strength of the R salt is calculated and diluted to N/20 by addition of the calculated amount of water.

### Estimation of primary amines

(a) **By diazotisation.** A known weight of the primary amine (1 g. for aniline or any of the toluidines) is dissolved in dilute hydrochloric acid sufficient to dissolve the amine, cooled and the solution diluted with water so as to have roughly a strength of N/10. The solution is cooled to 0° by adding washed ice and the nitrite solution run in till (after standing for some time) a drop of the solution gives a distinct and permanent reaction with starch iodide paper.



Let the volume of nitrite taken be V c.c. (N/2).

1 litre of N NaNO<sub>2</sub>  $\equiv$  — NH<sub>2</sub>, i.e., 16 g.

1 c.c. of (N/2) NaNO<sub>2</sub>  $\equiv$  8/1000 i.e., .008 g. of amino group.

$$\therefore \% \text{—NH}_2 \equiv \frac{V \times .008 \times 100}{W}$$

where W = weight of the amine taken.

(b) **By diazotisation and coupling.** 1 g. of the amine is diazotised exactly as in (a), 8 g. of sodium carbonate are added to the diazo solution and dissolved by stirring. The solution is cooled and N/20 R salt run in till the reaction is complete, the end point being determined by the absence of any colour in the out-spread as described under standardisation of R salt.

1 litre of N/20 R salt solution  $\equiv$  .8 g. of  $-\text{NH}_2$  group.

1 c.c.  $\equiv$  .0008 g. of  $-\text{NH}_2$  group.

If V be the volume of N/20 R salt used up by a gram of the amino compound, then the

$$\% \text{NH}_2 \equiv V \times .0008 \times 100$$

$$\equiv V \times .08$$

(Aniline, *p*-toluidine, *p*-nitraniline, etc., can be used.)

### 13. Estimation of the number of hydroxyl groups present in a phenol or an alcohol.

**Principle.** The number of hydroxyl groups in a phenol or alcohol is determined by preparing the acetyl derivative by the usual methods and hydrolysing a known weight of the acetyl derivative with a non-volatile acid like benzene sulphonic acid or toluene sulphonic acid. The liberated acetic acid is volatilised in a current of steam and is estimated by standard baryta.

**Preparation of benzene sulphonic acid.** The strength of the bench dilute sulphuric acid is first carefully determined by titration with standard baryta. 50 grams of pure barium benzene sulphonate are placed in a round-bottom flask, a little water is added to moisten it and the salt is subjected to steam distillation till the distillate is quite neutral. The volume of sulphuric acid required to liberate the benzene sulphonic acid is calculated (58 c.c. of 4N acid are required) and the excess of sulphuric acid if any is removed by adding baryta drop by drop till no precipitate of barium sulphate is formed. It is necessary that there should be no free sulphuric acid. The solution is filtered after allowing the precipitate to settle. The precipitate is washed with distilled water once or twice and the solution of benzene sulphonic acid diluted so that the strength of the acid is about 10-15%.

**Procedure.** 0.2 to 0.5 g. of the acetyl derivative is placed in a litre round-bottom flask fitted (Fig. 51) as if for steam distillation with an inlet for steam, the outlet for vapour being an alkali trap (splash-head). The object of the splash-head is to prevent any mechanical carrying over of the free benzene sulphonic acid along with the acetic acid liberated. The splash-head is connected to a Liebig's condenser to which is attached a two-litre flask for collecting the distillate, which should be protected

from atmospheric carbon dioxide by a soda-lime guard tube. It

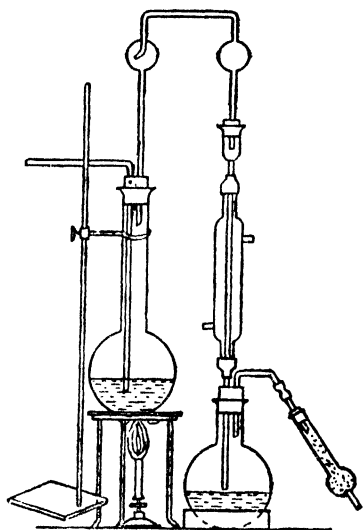


Fig. 51. Apparatus for estimation of hydroxyl group.

is better to use distilled water in the steam can but if tap water is used, steam should be allowed to escape for fifteen minutes. 100 c.c. of benzene-sulphonic acid solution are introduced into the flask containing the weighed substance and steam is blown through the flask at such a rate that about 300 c.c. of distillate collect per hour. The time taken for the process is about 3 to 4 hours. The distillation should be carried on till a few drops tested with litmus paper do not show an acid reaction. The entire distillate is titrated with standard baryta using phenolphthalein as indicator. A correction has to be applied

for carbon dioxide if the soda-lime guard tube is not used. A volume of distilled water equal to the volume of the distillate is titrated against the same baryta and this volume of baryta deducted from the titre value.

Let  $W$  = weight of acetyl derivative,  
and  $m$  = weight of acetic acid liberated.

Then the weight of acetyl derivative liberating one equivalent

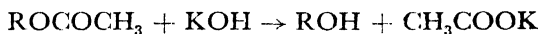
$$\text{of acetic acid} = \frac{W}{m} \times 60.$$

Hence the weight of the hydroxy compound containing

$$\begin{aligned} \text{one OH-group} &= \frac{W}{m} \times 60 - 43 + 1 \\ &= \frac{W}{m} \times 60 - 42 = x \text{ (say).} \end{aligned}$$

If the molecular weight of the hydroxy compound be  $M$ ,  
then the number of hydroxyl groups  $= \frac{M}{x}$ .

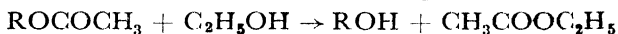
**Method II.** The acetyl derivative is refluxed with a known volume of alcoholic potash (N/2) and the excess of alkali determined by titration with standard HCl (N/2). 0.2 to 0.3 g. of the acetyl derivative is used and the experimental procedure is identical with that outlined under "estimation of esters," a blank being run simultaneously. The hydrolysis of the acetyl derivative is represented by the equation :



#### 14. Estimation of Acetyl groups

(A. G. PERKIN'S METHOD.)

**Principle.** The acetyl derivative is hydrolysed in the presence of alcohol with concentrated sulphuric acid and the ethyl acetate formed is absorbed in standard alcoholic potash



The method is not applicable to acetyl derivatives of amines.

**Procedure.** A distilling flask (250 c.c.) with its side tube bent is fitted to a long water-cooled condenser as shown in Fig. 52. About 0.5 g. of the acetyl derivative is taken in an ignition tube ( $4'' \times \frac{1}{2}''$ ) and the substance transferred with the tube slightly inclined so that it falls directly on to the bottom of the flask. The

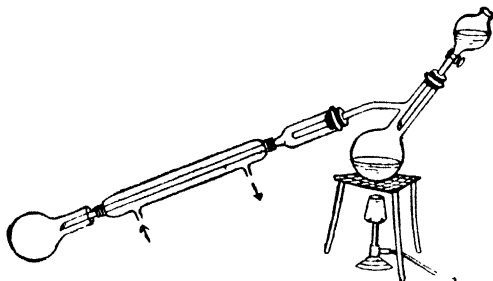


Fig. 52

difference in weight of the tube gives the weight of the substance transferred. Any particles adhering to the sides are washed down by 5 c.c. of strong sulphuric acid delivered from a pipette. Thirty c.c. of absolute alcohol are let in little by little from a pipette, while the flask is gently swirled and cooled under the tap. A piece of porous porcelain is added and an adapter is attached to the condenser tube. The flask is fitted with a one-holed rubber stopper carry-

ing a tap funnel (50 c.c.) 20 c.c. of alcohol are placed in the funnel and 20 c.c. of N/2 alcoholic potash in the 200 c.c. round bottom flask surrounding the adapter. The flask is heated on a wire gauze with a Bunsen burner carrying a nose tap, and the alcohol is added at such a rate, that it equals the rate of distillation. The distillation is continued till about half the liquid has distilled over. There should be no carbonisation taking place. The receiver is attached to a vertical water-cooled condenser and boiled on the water bath for about half an hour, after which, the inner tube of the condenser is washed with a little water and the excess of alkali titrated against standard acid using phenolphthalein as indicator.

### Calculation

1 litre of N NaOH = 43 g. of acetyl group

1 c.c. = .043 g.

Let 20 c.c. of N/2 alkali be  $\equiv V_1$  c.c. of N.HCl.

Let the titre value of the reaction be  $V_2$

$\therefore V_1 - V_2 = V$  c.c. N acid in alkali  $\equiv w$  g. of the solution

% of acetyl group in the compound =  $\frac{V \times .043}{w} \times 100$

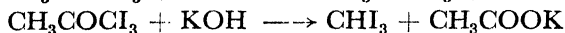
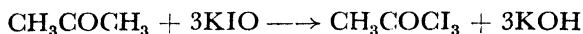
No. of acetyl groups =  $\frac{M}{x}$  where M = molecular weight,  $x$  =

wt. of compound containing 1 acetyl group.

( $\beta$ -Naphthyl acetate, hydroquinone diacetate, pyrogallol triacetate, acetyl vanillin have been found to give good results)

## 15. Estimation of Keto group.

**Estimation of acetone.** Iodine in alkaline solution reacts with acetone to form iodoform according to the equations,

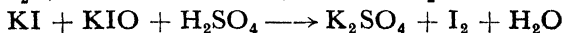
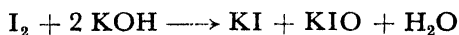


1 molecule of acetone (58 g.) = 3 molecules of iodine  
= 6 litres of N iodine

Hence 6 c.c. of N/10 iodine = .0058 g. of acetone.

1 c.c. of N/10 iodine = .00097 g. of acetone.

The excess of iodine maybe decomposed according to the equation :



and is titrated with thiosulphate.

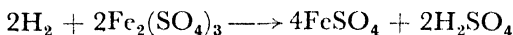
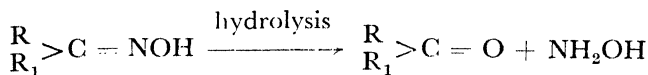
**Procedure.** About 2 g. of freshly-distilled acetone are dissolved in water and made up to 500 c.c. 15 c.c. of this solution are shaken with 50 c.c. of approximately N KOH in a 250 c.c. stoppered bottle. A known volume of iodine (about 100 c.c. of N/10) is added from a burette and the mixture shaken for about 15 minutes. It is then acidified with 50 c.c. of roughly N  $\text{H}_2\text{SO}_4$  and the excess of iodine liberated is titrated with N/10 thiosulphate. The amount of iodine which has interacted is determined by difference.

$$\text{Percentage purity of acetone} = \frac{V \times .00097 \times 500 \times 100}{15 \times W}$$

where  $V$  = volume of N/10 iodine which has been used up.

**Estimation of ketones which form a solid oxime.** The oxime is prepared by the usual methods and 0.1 g. of the dry oxime is weighed into a round-bottom flask of 250 c.c. capacity, 30 c.c. of dilute sulphuric acid (1 : 1) are added and 20 c.c. of a concentrated solution of ferric alum. Sufficient sulphuric acid should be present to prevent hydrolysis of the alum. The flask is fitted with an air condenser and the contents boiled for half to one hour, cooled and titrated against standard permanganate.

### Calculation



Hence the weight of oxime which requires 2 litres of N  $\text{KMnO}_4$  contains one keto group.

If  $W$  be the weight of oxime taken and  $V$  c.c. of N  $\text{KMnO}_4$  are required to react with the ferrous salt formed, then the weight of oxime containing one keto group

$$= \frac{W \times 2000}{V} = m \text{ (say).}$$

$\therefore$  The weight of ketone containing one  $>\text{CO}$  group =  $m - 15$ .

Hence the number of keto groups present in the compound

$$= \frac{\text{Molecular weight}}{m - 15}.$$



The oximes of acetophenone and benzophenone can be used for this experiment.

**Estimation of keto groups by preparing the semicarbazones and estimating, after hydrolysis, the ammonia liberated by the direct method.** (J. C. S. 1929, p. 1384).

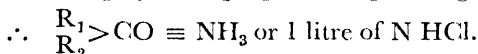
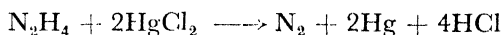
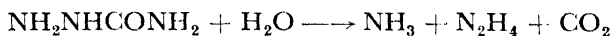
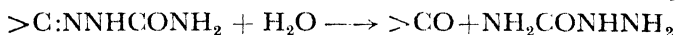
Solutions required :—

- (a) 15% hydrochloric acid (d. = 1.075).
- (b) 5% mercuric chloride solution.
- (c) 40% sodium hydroxide.
- (d) Saturated sodium thiosulphate.

**Procedure.** About 0.2 to 0.3 g. of the purified semicarbazone free from semicarbazide and other substances likely to give ammonia on hydrolysis, is weighed into a Kjeldahl flask of 500 c.c. capacity fitted with a reflux condenser and hydrolysed by heating for 6 to 7 hours with 50 c.c. of mercuric chloride and 40 c.c. of hydrochloric acid. The mercuric chloride is added only to decompose the hydrazine formed during hydrolysis.

After hydrolysis the flask is fitted up for ammonia distillation and the ammonia liberated by adding 40% sodium hydroxide mixed with an equal volume of saturated sodium thiosulphate for decomposing the mercury ammonium complex, until the solution is distinctly alkaline. The flask is then heated and the ammonia received in a known volume of an excess of standard HCl (N/2). When more than half the liquid has distilled over, the heating is stopped and the excess of acid is titrated. From the amount of ammonia liberated the weight of ketone containing one semicarbazone group can be calculated.

The reactions are as follows :—



If W be the weight of the semicarbazone taken and V c.c. of N HCl are required to neutralise the ammonia, then the weight of compound containing one semicarbazone group

$$= \frac{W \times 1000}{V} = m.$$

Then weight of compound containing one keto-group =  $m - 57$ .

$$\begin{aligned} \text{Hence the number of keto groups} &= \frac{\text{Molecular weight}}{\text{Wt. contg. one keto group}} \\ &= \frac{M}{m - 57} \end{aligned}$$

## 16. Estimation of Methoxyl groups

**Zeisel's method modified by Perkin.** The compound is heated with concentrated hydriodic acid and the methyl iodide so produced is carried over by a stream of carbon dioxide and absorbed in a solution of alcoholic silver nitrate. The silver iodide precipitated is then weighed.



**Hydriodic acid.** The density of the acid should be 1.7 corresponding to the constant boiling mixture, b.p. 127°. The strongest acid of d, 1.94 can be diluted with water and used. For every 25 g. of the acid 4 c.c. of water are to be added. Red phosphorus is likely to give off volatile impurities and therefore is boiled with 10% caustic potash till free from phosphoretted hydrogen, then filtered, washed free from alkali and preserved in distilled water.

**Alcoholic silver nitrate.** Two grams of silver nitrate are dissolved in 5 c.c. of water and then diluted with 45 c.c. of absolute alcohol. The solution is preserved in a well-stoppered bottle in the dark. It should be filtered and acidified with one drop of nitric acid immediately before use. For each estimation, 20 c.c. of the solution are taken in wash-bottle I and 15 c.c. in wash-bottle II.

**Procedure.** 0.2 to 0.3 g. of the substance is weighed accurately into a small tube. About 15 c.c. of the hydriodic acid are introduced into the Zeisel flask, and the tube containing the substance is gently slid into the flask. A few pieces of porous porcelain are added and the apparatus re-assembled as in Fig. 53. A very slow stream of carbon dioxide purified by passing through water and dried by concentrated sulphuric acid is passed at the rate of two bubbles per second, the leading-in tube being just over the surface of liquid instead of actually dipping into it. The flask is heated in a glycerine or metal bath gradually to 130°. The methyl iodide passing over, is freed from HI and iodine by a wash bottle containing red phosphorus suspended in water, and precipitates silver

iodide in the first absorption flask. When the upper portion of the liquid in the first flask is clear after the silver iodide has settled, the temperature of the bath is raised so as to boil very gently the hydriodic acid. After an hour the absorption flasks are disconnect-

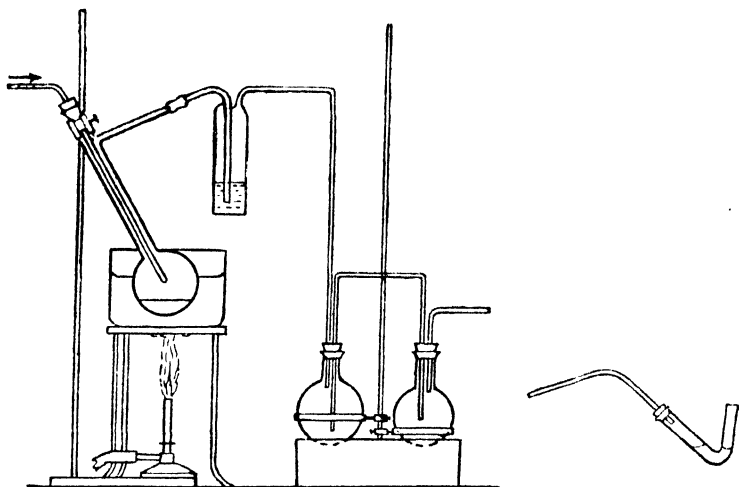


Fig. 53 Estimation of methoxyl.

ted and the gas led into a test-tube containing some of the silver nitrate. If no precipitate is seen in about five minutes the reaction is complete. The contents of the two wash-bottles are diluted with a little water, kept for a few minutes to ensure complete decomposition of the last traces of methyl iodide, and finally poured into 50 c.c. of boiling water acidified with nitric acid and boiled to drive off the alcohol. The precipitate is filtered in a glass crucible with sintered septum (I G 4) and dried at  $120^{\circ}$ .

$234.88 \text{ g. AgI} = 31.02 \text{ g. of methoxyl}$

$$\% \text{ Methoxyl} = \frac{W_1}{W} \times \frac{31.02}{234.9} \times 100 = x \text{ (say)}$$

where  $W$  = wt. of substance taken, and

$W_1$  = wt. of AgI formed.

Hence weight of substance containing one methoxyl group  $\left\} = \frac{100}{x} \times 31.02 = m \text{ (say)}$

Hence the number of methoxyl groups  $= \frac{M}{m}$

where  $M$  = molecular weight of the substance.

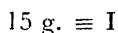
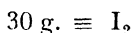
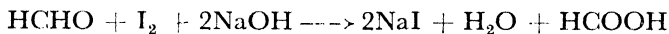
## 17. Estimation of Aldehydes

### Estimation of formaldehyde in commercial formalin.

About 3 g. of formalin are weighed into a 250 c.c. flask using the Lunge-Rey pipette and made up to the mark. 15 c.c. of the solution are mixed with 50 c.c. of N/10 iodine solution and 10% sodium hydroxide is added drop by drop from a burette till the liquid becomes light yellow in colour. After standing for about 15 minutes, 15 c.c. of 10% hydrochloric acid ( $d = 1.048$  at  $30^\circ$ ) are added and the liberated iodine is titrated with thiosulphate using starch as indicator. 1 c.c. of N/10 iodine = 1.5 m.g. of formaldehyde, i.e., .0015 g.

This method is very satisfactory for formaldehyde provided other aldehydes are absent. In a solution containing 1 g. of formaldehyde per litre two titrations should not differ by more than 0.1 c.c. of thiosulphate. Excess of alkali should be avoided.

### Reactions

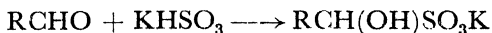


1 litre of N/10 iodine = 1.5 g. of formaldehyde.

1 c.c. = .0015 g.

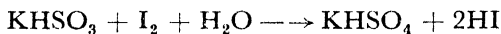
**Ripper's method.** Ripper (Chem. Soc. Abs. 1901, ii, 205) has described a general method for all aldehydes and some of the methyl ketones which form stable additive compounds with sodium bisulphate. The reaction depends on the fact that the bisulphite addition compounds unlike free sulphites are more stable and are not oxidised by a solution of iodine. The method is successful only when dilute solutions are employed. Decinormal iodine and potassium bisulphite (12 g. per litre) are required.

25 c.c. of the aldehyde solution (.5% aqueous or very dilute alcoholic) are added to 50 c.c. of the bisulphite solution contained in a shaking bottle, shaken well and left to stand for about 15 minutes. During this interval 50 c.c. of the bisulphite solution are titrated with iodine using starch as indicator.



The excess of the bisulphite in the aldehyde solution is then deter-

mined by means of the iodine solution. The difference between these two titrations give the iodine equivalent of the aldehyde present in the original solution.



$$\text{I} \equiv \frac{\text{KHSO}_3}{2} = \frac{\text{RCHO}}{2} = \frac{\text{M}}{2} \quad \text{where M is the molecular weight of the aldehyde.}$$

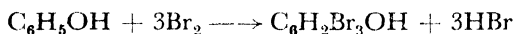
$$1 \text{ c.c. N/10 Iodine} = \frac{\text{M}}{20} \times \frac{1}{1000}$$

$$\text{The weight of aldehyde in 25 c.c. solution} = \frac{\text{V} \times \text{M}}{20 \times 1000}$$

where V = volume of N/10 iodine solution equivalent to bisulphite used up and M = molecular weight of the aldehyde. Use dilute acetaldehyde solution, or benzaldehyde freshly distilled.

### 18. Estimation of Phenol

The determination depends on the formation of tribromophenol according to the following equation :



Instead of using a standard solution of bromine, a bromate-bromide mixture which readily liberates bromine in the presence of an acid is preferable as its strength does not vary. The brominating solution (N/10) is prepared by dissolving 15 g. of potassium bromide and 2.78 g. of potassium bromate in a litre. It is standardised by adding an excess of 15-20% potassium iodide, acidifying and titrating the iodine liberated with standard thiosulphate (N/10).

1 c.c. of N/10 thiosulphate  $\equiv$  1 c.c. of N/10 Br.

$$\equiv \frac{\text{C}_6\text{H}_5\text{OH}}{6 \times 10000} \equiv \frac{94}{60000} \equiv 0.001567 \text{ g. of phenol.}$$

**Procedure.** A solution of freshly distilled phenol, roughly N/10 (1.57 g. per litre) is prepared and 20 c.c. of it are measured into a 300 c.c. stoppered bottle. 50 c.c. of water and 5 c.c. of concentrated hydrochloric acid are added and the brominating solution run in from a burette till a permanent yellow colour is produced after shaking. About 2 c.c. of 15% potassium iodide solution are added and the iodine liberated by the excess of bromine is titrated against standard thiosulphate as usual, using starch as indicator.

Let V be the volume of bromate-bromide mixture added.

Let  $x$  be the volume of thiosulphate  
 $\equiv 20$  c.c. of brominating solution.

Then  $V$  c.c. of bromate-bromide mixture

$$\equiv \frac{x}{20} \times V \text{ of thiosulphate.}$$

Let  $y$  be the thiosulphate required for the excess of bromine.

Hence, the amount of bromine that reacted

$$\equiv \left( \frac{V}{20} \times x - y \right)$$

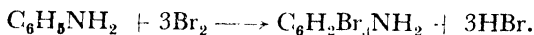
Hence, phenol present in 20 c.c. of solution

$$= \left( \frac{V}{20} \times x - y \right) \cdot 0.01567 \text{ g.}$$

Hence, phenol present in 1 litre of solution

$$= 50 \left( \frac{V}{20} \times x - y \right) \cdot 0.01567 \text{ g.}$$

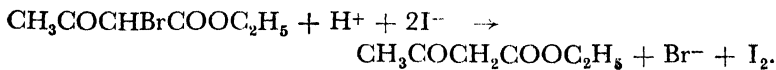
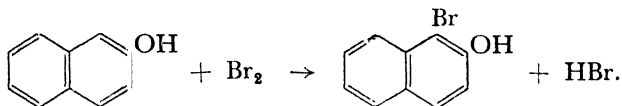
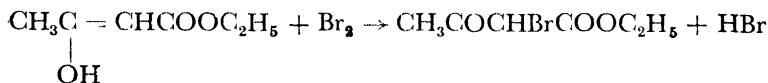
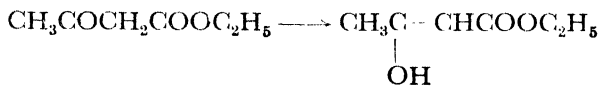
Aniline can be estimated by the same method, the reaction taking place according to the following equation :



## 19. Determination of percentage of Enol

### K. H. Meyer's method.

In order to determine the percentage of enol in an equilibrium mixture, advantage is taken of the fact that the enol form reacts with bromine very rapidly compared with the keto. Taking acetoacetic ester the following reaction takes place.



1 mol. of iodine  $\equiv$  1 mol. of enol  $\equiv$  130 g.  $\equiv$  2 litres N. thio-sulphate.

2 litres of N/10 thiosulphate  $\equiv$  13.0 g.

1 litre of N/10 thiosulphate  $\equiv$  6.5 g.

1 c.c. of N/10 thiosulphate  $\equiv$  .0065 g. of the enol.

**Procedure.** Required.

- (1) An approximately N/10 alcoholic bromine (cooled in ice).
- (2) Potassium iodide 10% solution.
- (3) Sodium thiosulphate 0.1 N
- (4)  $\beta$ -Naphthol 5% alcoholic solution.

1.625 g. of the ester are dissolved in 100 c.c. of alcohol in a 500 c.c. w.m. conical flask and cooled to  $-7^{\circ}$  in a freezing mixture. The contents are given a swirling motion and ice-cold alcoholic bromine solution (about 21 c.c.) is added till a faint yellow colour is produced. Alcoholic  $\beta$ -naphthol is added at once in sufficient amount to remove the colour due to excess of bromine. The time for addition of bromine and the  $\beta$ -naphthol should not exceed 20 seconds. 5 c.c. of the potassium iodide are added next quickly and the liberated iodine titrated against standard thiosulphate using starch as indicator.

If V be the volume of 0.1 N thiosulphate used and w the weight of ester taken then the % enol  $= \frac{100 \times V \times .0065}{w}$

Due to the fact that  $\beta$ -naphthol solution in alcohol is coloured brown, a certain amount of difficulty is experienced in ascertaining the point at which the excess of bromine is removed. An error is also caused during the titration with thiosulphate in ascertaining the final stage of disappearance of the yellow colour due to iodine; by using diisobutylene (easily available) which absorbs bromine with formation of a colourless bromide, the above difficulties are overcome.

**Required.**

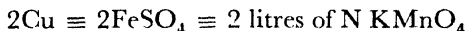
1. Absolute methanol (distilled over quicklime)
2. Approximately N/10 bromine in absolute methanol (2 g. dry bromine in 250 c.c. of methanol to be freshly prepared)
3. 0.1 N thiosulphate
4. 10% potassium iodide solution
5. Starch solution
6. Diisobutylene.

**Procedure.** About 0.2 to 0.3 g. of pure dibenzoylmethane is weighed into a wide-mouthed conical flask of 250 c.c. capacity containing 25 to 30 c.c. of absolute methanol. After the compound has dissolved the flask is cooled to  $-5^{\circ}$  in a freezing mixture of ice and salt and the cooled alcoholic bromine (25 c.c.) is added. The solution is thoroughly mixed and almost immediately a slight excess of diisobutylene (3 to 5 c.c.) is added to absorb the excess of bromine. The time interval for adding the bromine and absorbing the excess should not exceed 15 seconds (a stop-watch may be used). 5 c.c. of the potassium iodide are then added, and the mixture brought up to the room temperature (about  $30^{\circ}$ ) by dipping in hot water and swirling. The liberated iodine is titrated after 5 minutes keeping, with standard thiosulphate till the colour becomes yellow, then diluted with water, 5 c.c. of starch are added and the titration completed as usual. The % of enol is calculated as above.

1 litre of N iodine or thiosulphate  $\equiv \frac{1}{2}$  g. mol. of this substance.

## 20. Estimation of Sugars.

**Bertrand's method.** The method consists in boiling a known volume of the sugar solution with excess of alkaline copper hydroxide. The precipitated cuprous oxide is dissolved in a warm acid solution of ferric alum. The ferrous sulphate formed by reduction is titrated with standard permanganate.



1 atom of copper, i.e., 63.6 g.  $\equiv$  1 litre of N  $\text{KMnO}_4$

1000 c.c. N/10  $\text{KMnO}_4 \equiv 6.36$  g. of copper

1 c.c.  $\equiv .00636$  g., 6.36 m.g.

By reference to the tables the weight of the particular sugar corresponding to the values can be found out

### Solutions required :—

(A) **Copper solution.**

Cupric sulphate, 40 g. in 1 litre of solution.

(B) **Alkaline tartrate.**

Rochelle salt, 200 g.

Caustic soda, 150 g.

} dissolved in water and  
made up to a litre.



- (C) **Acid ferric sulphate.** }  
 Ferric alum, 120 g. } made up to 1 litre.  
 Concentrated sulphuric  
 acid 100 c.c. }
- (D) **Permanganate solution.**

5 g. of potassium permanganate dissolved in 1 litre of solution.

A preliminary test should be made if the ferric alum solution reduces permanganate. If it does, permanganate should be added drop by drop till a faint colour persists.

**Procedure.** 20 c.c. of the sugar solution (which may contain sugar up to 100 m.g.) are taken in a conical flask of 250 c.c. capacity and 20 c.c. of copper sulphate solution are added followed by 20 c.c. of the tartrate solution. The solution is heated gradually to boiling and maintained at this temperature



Fig. 54  
Allihn  
filter tube.

for 3 minutes, after which the precipitate of cuprous oxide is allowed to settle for a few seconds. The supernatant liquid is filtered through an Allihn filter (Fig. 54) with glass sintered septum (IG4) having a thin layer of Gooch asbestos. The filtrate should be coloured showing excess of copper. As little of the cuprous oxide as possible should be transferred to the filter, as a quick solution of the oxide in acid-iron mixture is otherwise not possible. The precipitate is washed twice with a little water, allowed to settle and filtered as before. The filter flask is connected to the pump, exhausted, the filtrate is discarded and the flask thoroughly cleaned with distilled water. To the flask containing the cuprous oxide enough of the ferric solution is added to dissolve the oxide completely. The solution assumes a clear green colour and it is poured on to the filter which contains a little of the undissolved oxide and the filtrate received in the filter flask. The original flask and the filter are washed with water and the combined filtrate and washings are titrated against standard permanganate till a permanent pink colour is obtained.

From the titre value the amount of sugar can be calculated thus :

Volume of sugar solution taken = 20 c.c.

Volume of N/10 permanganate required to react with the  
ferrous sulphate formed =  $x$  c.c.

Copper equivalent of sugar =  $x \times 6.36$  milligrams.

Sugar content corresponding to the copper equivalent  
=  $m$ . milligrams (from the  
tables)

$\therefore$  20 c.c. of the sugar solution contain  $m$  milligrams.

Use pure glucose for the estimation of a reducing sugar by  
this method.

Amounts of Copper precipitated by different amounts  
of various reducing sugars.

## GLUCOSE

Sugar in m.g.	Copper in m.g.	Sugar in m.g.	Copper in m.g.	Sugar in m.g.	Copper in m.g.
10	20.4	41	79.3	71	131.4
11	22.4	42	81.1	72	133.1
12	24.3	43	82.9	73	134.7
13	26.3	44	84.7	74	136.3
14	28.3	45	86.4	75	137.9
15	30.2	46	88.2	76	139.6
16	32.2	47	90.0	77	141.2
17	34.2	48	91.8	78	142.8
18	36.2	49	93.6	79	144.5
19	38.1	50	95.4	80	146.1
20	40.1	51	97.1	81	147.7
21	42.0	52	98.9	82	149.3
22	43.9	53	100.6	83	150.9
23	45.8	54	102.3	84	152.5
24	47.7	55	104.1	85	154.0
25	49.6	56	105.8	86	155.6
26	51.5	57	107.6	87	157.2
27	53.4	58	109.3	88	158.8
28	55.3	59	111.1	89	160.4
29	57.2	60	112.8	90	162.0
30	59.1	61	114.5	91	163.6
31	60.9	62	116.2	92	165.2
32	62.8	63	117.9	93	166.7
33	64.6	64	119.6	94	168.3
34	66.5	65	121.3	95	169.9
35	68.3	66	123.0	96	171.5
36	70.1	67	124.7	97	173.1
37	72.0	68	126.4	98	174.6
38	73.8	69	128.1	99	176.2
39	75.7	70	129.8	100	177.8
40	77.5				

### **Polarimetric estimation of cane sugar (sucrose) in the presence of glucose (dextrose).**

The method adopted, usually called that of double-polarisation, depends on the fact that when sucrose is heated with a dilute mineral acid it undergoes hydrolysis with the formation of equal quantities of dextrose and laevulose. Since the laevo-rotation of the latter is greater than the dextro-rotation of the former, the reaction is usually known as inversion of cane sugar and the product is termed invert sugar. The change in rotation is a measure of the amount of sucrose originally present. 10-15 g. of the mixed sugars, if solid, are dissolved in water or the volume, if it is in solution, is made up to 100 c.c. in a measuring flask. 50 c.c. of the solution are pipetted into a 100 c.c. flask, 5 c.c. of concentrated hydrochloric acid are added, a thermometer is dipped into the solution and the flask heated on a water-bath with constant shaking, the rate of heating being so regulated that the solution reaches a temperature of  $67^{\circ}$  to  $70^{\circ}$  in  $2\frac{1}{2}$  minutes. The solution is kept at this temperature for about 5 minutes, then rapidly cooled and made up to 100 c.c. The rotation of the inverted sugar solution is determined using a 200 m.m. tube and a sodium flame or the sodium arc lamp, if available. Since in this solution only half the weight of the sugar originally present has been used, the reading obtained should be doubled. With the remainder of the original solution the rotation due to both glucose and sucrose is determined and the calculation made by solving the two simultaneous equations as shown below.

#### **Calculation**

Let  $x$  be the amount of cane sugar and  $y$  that of glucose.

Let  $a_1$ ,  $a_2$  and  $a_3$  be the specific rotations of cane sugar, glucose and invert sugar at the temperature  $l$  of observation.

Let  $A$  and  $B$  be the observed rotations before and after the inversion.

342.2 g. of cane sugar give 360.2 g. of invert sugar.

1 g.     ,,     ,,     gives  $\frac{360.2}{342} = 1.052$  g. of invert sugar.

Then

i.  $l [x \times a_1 + y \times a_2] = A$ , where  $l$  is the length of the observation tube.

ii.  $l [-x \times 1.052 \times a_3 + y \times a_2] \equiv B$ .  $a_3$  being negative is taken numerically.

Hence,

$$\text{i--ii, i.e., } l \times x (a_1 + 1.052 a_3) = A - B$$

$$\therefore x = \frac{A - B}{l (a_1 + 1.052 a_3)}.$$

Temperature is an important factor as the rotations of the various sugars vary with temperature.

Cane sugar 
$$[\alpha]_D^t = 66.67 - .0247 (t - 20)$$
  
 where  $t$  = temperature  
 of observation.

Invert sugar 
$$[\alpha]_D = -19.447$$
  

$$[\alpha]_D^{25} = -18.39$$
 ; i.e. change per degree is  
 $0.0114^\circ$  less, numerically.

Glucose (dextrose) 
$$[\alpha]_D^{20} = 52.7$$
  

$$[\alpha]_D^{25} = 52.48$$
, i.e.  $0.044^\circ$  less per degree.

### Estimation of glucose by the method of Lane and Eynon.

**1. Preparation of Fehling's solution.** The Fehling's solution employed is that known as Soxhlet's modification and is prepared by mixing equal volumes of solutions A and B :—

A. 34.639 g. of pure crystallised copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is dissolved in distilled water and made up to 500 c.c. B. 173 g. of Rochelle salt and 50 g. of sodium hydroxide are dissolved in distilled water and made up to 500 c.c. Equal volumes of A and B are mixed just when needed. The indicator is made by dissolving 1 g. of methylene blue in water and making up to 100 c.c.

**2. Preliminary titration.** 10 or 25 c.c. of the Fehling's solution in a 400 c.c. conical flask is treated cold with 15 c.c. of the sugar solution and without further dilution heated to boiling over a wire gauze. After the liquid has been boiling for about 15 seconds it will be possible to judge if the copper is almost reduced by the bright red colour imparted to the boiling liquid by the suspended cuprous oxide. If it is judged that nearly all the copper is reduced, a few drops of the methylene blue indicator are added, boiling is continued for 1-2 minutes after ebullition and then the sugar solution is added in small quantities, say 1 c.c. or less at a time, the liquid being allowed to boil for 10 seconds between each addi-

tion until the colour of the indicator is completely discharged. If after the mixture of Fehling's solution with 15 c.c. of the sugar solution has been boiling for about 15 seconds there appears to be still much unreduced copper, a further 10 c.c. of sugar solution is added and the whole allowed to boil for 15 seconds and so on until it is considered unsafe to add a further large increment of sugar solution; boiling is then continued for 1-2 minutes, after which the indicator is added and the titration is completed by small additions of the sugar solution. It is advisable not to add the indicator until the neighbourhood of the end point has been reached.

**3. Standard method of titration.** 10 or 25 c.c. of the Fehling's solution is measured in to a flask of 400 c.c. capacity and treated cold with almost the whole of the sugar solution (determined in the preliminary titration) required to effect reduction of all the copper so that if possible not more than 1 c.c. is required later to complete the titration. The flask containing the cold mixture is heated over a wire gauze ; after the liquid has begun to boil it is kept in moderate ebullition for 2 minutes and then without removal of the flame, 3-5 drops of the methylene blue indicator are added, and the titration is completed in 1 minute further, so that the reaction liquid boils altogether for 3 minutes without interruption. The indicator is so sensitive that the end point can be determined to within 1 drop of the sugar solution in many cases. The amount of glucose can be determined by reference to the table below. Other sugars like maltose, lactose, fructose and invert sugar (obtained by hydrolysis of sucrose) can be estimated by the same method. Fuller details can be obtained by reference to the original paper by Lane and Eynon (J. S. C. I. 1923, 42, 321')

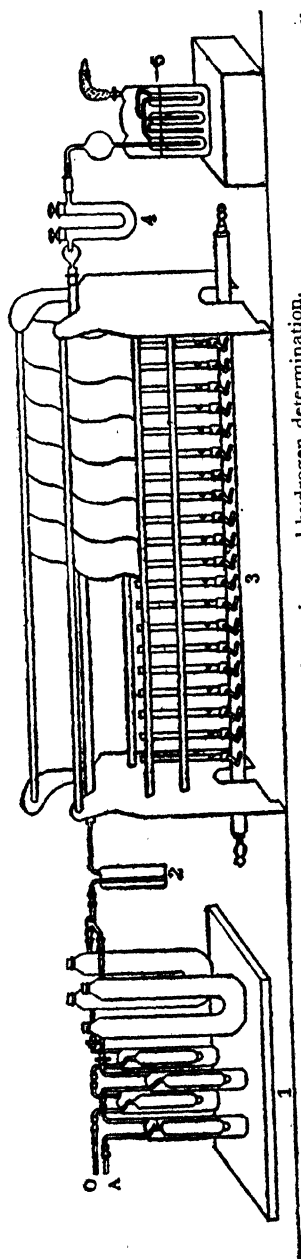


Fig. 55. Combustion furnace for carbon and hydrogen determination.  
(1) Drying and purifying train. (2) Bubbler. (3) Combustion furnace. (4) Calcium chloride absorption tube. (5) Potash bulb

about 15" high the limbs of which are alternatively filled with calcium chloride and soda-lime. The drying and purifying trains are connected by a Y-tube to a common bubble counter (2) containing concentrated sulphuric acid and thence to the combustion tube.

The object of the bubbler is not only to give an idea of the rate of passage of the gas through the apparatus but also to indicate the relationship between the gas entering the combustion tube and the amount leaving the potash bulb. The rate of passage of gas is controlled by means of screw clamps interposed between the gas holders and the drying train as well as by a stop-cock placed after the bubble counter.

**Combustion tube and furnace.** The type of furnace generally used (3) consists of a series of Bunsen burners of the Teclu pattern numbering 14 or 15 provided with flame spreaders and screwed on to a common gas feed. Each burner is an independent unit by itself having its own gas and air regulators. The flame from these burners impinges on an iron or nickel trough inside which is placed a thin asbestos paper on which the combustion tube rests. A row of fireclay tiles serving as muffles, covers the combustion tube on either side and helps in the regulation of temperature.

Gas-heated combustion furnaces are now being replaced by electrically heated furnaces with multiple heaters, generally three, each controlled by its own rheostat. The heaters which are of different dimensions, completely enclose the combustion tube and move on wheels sliding over steel rods so that any portion of the tube may be heated. The heaters are built in two sections which are hinged so as to permit of being opened out for inspecting the combustion tube at any stage.

The combustion tube is made of the hardest combustion glass with an internal diameter of 15 mm. and a thickness of 2 mm. The length of the combustion tube is 3 feet, i.e., 75 cm. allowing a projection of 5 cm. at either end of the furnace, the effective heating surface being about 65 cm. These tubes are sold in cut lengths, and, if necessary, can be cut of sufficient length from a longer tube. The edges should be rounded and the tube thoroughly cleaned and air dried.

**Filling the tube.** The elements present in the substance should first be qualitatively detected and the filling then decided

on. When carbon, hydrogen and oxygen alone are present, the tube can be filled thus : A loose plug of ignited asbestos wool or a roll of copper gauze, 0.5 cm. wide so as to just fit into the tube, is pushed in and kept at a distance of 5 cm. from one end. Pure wire-form cupric oxide, heated previously in a porcelain basin over a Techlu burner and cooled in a desiccator, is poured through a wide funnel into the tube held vertically, so as to fill a length of about 45 cm. A second plug of copper gauze is pushed in to keep the copper oxide in position. A space of about 6-7 cm. is left for a porcelain boat. A roll of copper gauze 15 cm. long is wound round a stout copper wire longer than the wire gauze till the roll nearly fits the tube. The projecting ends of the wire are bent into loops to facilitate easy introduction and withdrawal. The spiral is oxidised by heating strongly in a blast lamp, cooled in a desiccator and then pushed into the tube to a distance of 5 cm. from the other end. The loops enable it to be moved backward and forward by hooking with a bent glass rod or stout copper wire. The combustion tube is next fitted with good one-holed tight fitting rubber stoppers carrying short pieces of glass tubing which are flush with the narrow end of the stoppers. The portions of the corks coming in contact with the combustion tube are smeared with a *trace* of vaseline or glycerine to prevent their sticking to the glass.

The tube is laid on the trough of the furnace, and a piece of asbestos board  $1/8$  in. thick with a circular hole is placed on each end to protect the rubber stoppers from the heat of the furnace during combustion.

**Absorption tubes.** As absorbent for water, granular calcium chloride or pumice moistened with concentrated sulphuric acid is used, the latter being generally preferred. A U-tube with stop-cocks having a bulb on one limb (4) is the one universally employed. Granular calcium chloride should be heated previously in a porcelain basin to drive off moisture and cooled in a desiccator containing calcium chloride similarly heated. The calcium chloride is sieved from fine dust, placed in the U-tube to a height of about 1-2 cm. below the stop-cocks and wad of cotton wool, placed above it. Since calcium chloride contains basic chlorides which absorb carbon dioxide, a stream of dry carbon dioxide from a Kipp is passed through the U tube for two hours before use and the excess of the gas is afterwards driven out by a current of dry air. This process has to be repeated till constant weight is reached.



For the other absorbent, pieces of pumice about the size of a pea are sieved, treated with hydrochloric acid to remove carbonate, washed thoroughly with water and then dried in a porcelain basin by heating over a free flame. The dried pumice is placed in the U tube and then soaked in sulphuric acid for about three to four hours, the excess of acid is drained away and the side tube cleaned by an asbestos thread, and finally by cotton wool.

**Potash bulbs.** The form of potash bulb (5) used is shown in Fig. 55. The caustic potash solution is made by dissolving 50 g. of pure pellets in 50 c.c. of water. To fill the bulb, the detachable side-tube is removed and a rubber tube is attached. The other end is allowed to dip into a basin containing the potash solution and suction is applied till the bulbs are nearly full. The ground glass joint is faintly vaselined and the side-tube filled half with soda-lime and half with calcium chloride, is replaced. When not in use the ends are closed by pressure tubing plugged with glass rods. The calcium chloride U-tube and the potash bulb are kept in a small wooden box with grooves cut in for the convenience of transport to the balance. In connecting up the combustion tube to the absorption tubes, the calcium chloride is placed first and then the potash bulb, pressure tubing being used for connection and glass to glass joint being secured.

The potash bulb is connected to another small U-tube half filled with soda lime and half with granular calcium chloride which serves as a guard tube and which is finally connected to a gas-washing bottle containing concentrated sulphuric acid, to prevent ingress of moisture or acidic vapours to the combustion tube, cupric oxide being especially hygroscopic.

**Preliminary heating of the combustion tube.** With the absorption tubes disconnected and protected as described, the rubber stopper at the exit end is removed, air is turned on and its rate of flow adjusted so that two or three bubbles per second pass through the bubbler. The burners are lighted and the combustion tube gradually raised to a dull red heat at which it is maintained for an hour or more, with the tiles completely covering the tube. Moisture collects at the free end and can be removed by pieces of filter paper. When no more condensation of moisture takes place, the rubber stopper with the guard tube is replaced and heated for a further period of an hour or so, after

which the current of air is cut off. The burners are turned down and while the apparatus is cooling the absorption tubes are weighed.

**Weighing the absorption tubes.** The absorption tubes are wiped with a clean cloth, taking care that vaseline from the stop-cocks is not removed during the process, and left in the balance case for about half an hour prior to weighing.

**Blank experiment.** The guard tube is removed, the absorption apparatus connected to the combustion tube and the entire system tested for air-tightness as follows : a piece of rubber tubing with a screw-clip is attached to the potash bulb and a stream of air is allowed to bubble through the apparatus. If the rate of bubbling is the same through the bubble counter and the potash bulb, the air meets with no obstruction as it passes ; otherwise, the combustion tube should be tapped gently to make a passage for the gas. The screw-clip is now closed and the air turned on to its full pressure. If after the escape of the first few bubbles, no gas should pass through the apparatus, the system may be considered to be air-tight. The screw-clip is released, the guard tube is attached to the potash bulb, and with the air flow adjusted at 2-3 bubbles per second, the tube is gradually heated to a dull red heat for half an hour. The absorption tubes are disconnected, stoppered, and the guard tube is attached once again to the combustion tube. The flame is turned down and the absorption tubes weighed as before. The increase in weight should not exceed .0004 g. ; otherwise the blank should be repeated till constant weight is reached within the stated limits.

**Drying of substances before analysis.** Ordinarily, substances to be combusted should be dried in a vacuum desiccator which keeps its vacuum overnight and is evacuated with a good pump. Substances which contain water or other solvent so firmly bound that it cannot be removed in a vacuum at room temperature, are heated in the "drying pistol" (Fig. 7a). The vapour of the liquid in the boiling flask heats the wide inner tube in which the substances is kept in a boat or a specimen tube. The inner tube is connected by a ground glass joint to a small retort with a side tube having a stop-cock for connection to a pump and containing a drying agent (phosphorus pentoxide for water and alcohol and paraffin wax for absorbing other vapours). The inner tube with the retort is kept evacuated during drying. The

bath liquid to be used depends on the melting point of the substance. Generally chloroform, water, toluene or xylene can be employed. Toluene (b.p.  $110^{\circ}$ ) is most commonly used.

**Weighing the boat and the substance.** A porcelain boat is cleaned by boiling with nitric acid, washed with water, heated carefully on a blast lamp and cooled in a desiccator, the boat being placed in a groove cut in a big cork completely wrapped in tin foil. When cold it is weighed and 0.15 to 0.2 g. of the substance is weighed for analysis. It is then replaced in the desiccator. Sucrose, benzoic acid and acetanilide are suitable known substances to be used for practice analyses.

**Combustion.** The boat containing the substance is introduced into the combustion tube in a position close to the copper oxide, the oxidised copper spiral is pushed into its place and the apparatus connected up as before and tested for leaks. The column of copper oxide is heated at first gently commencing from the exit end by lighting the burners one by one up to a distance of about 10 cm. from the boat. The oxidised copper spiral is similarly heated with a low flame and a slow current of air at 3 bubbles per second is sent in. The boat containing the substance is heated by placing hot tiles over that portion of the tube and finally by lighting the burners below. It is necessary that the progress of all combustion is slow and regular. The indication that combustion has commenced is the appearance of moisture on the exit end and an increase in the speed of gas through the potash bulb. When the combustion is nearly finished as could be judged by the rates of bubbling in the bubbler and in the potash bulb, the air is quickly replaced by oxygen to prevent back diffusion. The tiles over the boat are closed and the whole tube heated to dull redness until all moisture is driven off from the exit end and the gas issuing from the apparatus is rekindled by a glowing splinter. The tiles over the boat should be occasionally raised to see if any carbon residue is left. Substances may sometimes leave a carbon residue (graphitic) which only burns off slowly and the heating should be continued till no residue is left. The final traces of moisture condensing at the exit end are driven into the absorption tube by placing a hot tile or asbestos board immediately near the part of the tube containing it. Care should be taken in this process not to burn the cork. The time taken for a combustion is about  $1\frac{1}{2}$  to 2 hours from the commencement of heating. As soon as the

combustion is over, the burners are turned down and the stream of oxygen replaced by air in order to displace oxygen from the absorption apparatus. After about half an hour, the absorption train is disconnected from the combustion tube and stoppered. The guard tube is once again attached to the combustion tube, the burners are extinguished and the air shut off. The absorption tubes are wiped free from dust, placed in the wooden box and weighed after keeping for an hour with the usual precautions. The percentages of carbon and hydrogen are calculated thus :

$$\text{Percentage of carbon} = \frac{\text{weight of carbon dioxide}}{\text{weight of substance}} \times \frac{3}{11} \times 100.$$

$$\text{Percentage of hydrogen} = \frac{\text{weight of water}}{\text{weight of substance}} \times \frac{1}{9} \times 100.$$

When the substance contains nitrogen, sulphur or halogen the filling of the combustion tube has to be modified thus :

**Nitrogen present.** The layer of copper oxide is reduced by about 10 cms. and a reduced copper spiral is placed in its stead. The spiral is prepared by rolling a strip of copper gauze, 12 cms. wide round a copper wire as in the case of oxidised copper spiral, and heated strongly to redness in the blast lamp. It is slipped into a hard glass test-tube containing 1-2 c.c. of methyl alcohol, the test tube being clamped to a stand. The vapours from the tube usually take fire and when the flame dies out, the test tube is fitted with a one-holed cork carrying a bent tube and connected to a suction pump to remove all alcohol. After about fifteen minutes, the spiral is removed and kept in a clean tube inside a vacuum desiccator. The spiral of copper serves to reduce any oxides of nitrogen formed. It is placed at the exit end after the layer of cupric oxide, just before the commencement of the actual combustion. The rest of the procedure is exactly as described.

**Sulphur or halogen present.** Chips of fused lead chromate can be placed inside the reduced copper spiral or the copper oxide layer may be reduced by half the original length and replaced by pieces of fused lead chromate (12 mesh). The following precautions have however to be observed : (1) the lead chromate should not be heated as strongly as the copper oxide ; (2) the column of lead chromate covered by the last three or four burners should not be heated too strongly as lead sulphate is likely to be decomposed and lead halide volatilised. The combustion of

halogen-containing substances may be carried out with copper oxide alone if a silver spiral is introduced at the exit end of the combustion tube to retain the halogen.

An improvement which helps one to carry out the combustion in a shorter time, consists in placing a layer of pumice impregnated with cerium dioxide to a length of about 5 cm. between the boat and the copper oxide layer.

### Estimation of nitrogen

There are two well-known methods for the estimation of the nitrogen content of an organic compound. These are (1) the absolute or gasometric method of Dumas involving the combustion of the organic compound, and (2) the titri-metric method of Kjeldahl.

The method of Dumas is the one ordinarily employed and it is almost universal in its application. The combustion is similar to that for carbon and hydrogen, but the operation has to be carried out in a current of carbon dioxide and the nitrogen evolved is collected over potash, its volume measured and its weight calculated. Since neither oxygen nor air can be employed to oxidise the substance, it is necessary to mix the substance intimately with an oxidising agent, viz., finely powdered pure cupric oxide usually of the wire-form, to ensure its complete combustion.

**Apparatus and details.** (1) Carbon dioxide generator. The carbon dioxide necessary for this purpose can be obtained from a Kipp but it is best to liberate it by heating pure sodium bicarbonate in a hard glass test-tube (1) and passing the gas through a safety wash-bottle containing sulphuric acid (2) which dries it and the same time indicates the rate of flow of the gas (Fig. 56).

(2) Filling the combustion tube. The combustion furnace and tube may be of identical dimensions as with carbon and hydrogen determination but it is an advantage to have the tube of a somewhat smaller bore. The oxidised copper gauze (A) as well as the reduced copper gauze (E) are kept in similar positions but the length of the reduced copper spiral is only 10 cms. The oxidised copper gauze may as well be replaced by a layer of coarse wire-form copper oxide of equal length. A plug of freshly ignited asbestos or a roll of copper gauze (1.5 cm.) moving under slight

pressure inside the combustion tube is introduced so that it is at a distance of about 15 cms. from one end of the tube. The tube is clamped vertically so that the longer part is above. Pure wire-form copper oxide which has been strongly heated in a basin and cooled in a desiccator is now poured through a funnel with a short wide stem so as to fill a length of about 35 cms. (D). Above this a 1 cm. layer of fine cupric oxide made by grinding the wire-form copper oxide and sieving (30-40 mesh) so as to remove coarser particles, is introduced. The tube is now pre-heated for about half an hour in a current of purified air or oxygen so as to burn away carbonaceous impurities, and expel any moisture at the same time, and allowed to cool. While the tube is cooling, 0.2 to 0.3 g. of the dry substance sufficient to liberate about 20 c.c. of nitrogen is weighed into a clean dry agate or glass mortar and about 16 g. of fine dry copper oxide is carefully added and mixed well with the pestle. The mixture (C) is poured into the tube through a dry short-stemmed funnel or even a thistle funnel so that no particles fly off. The mortar and pestle are washed thrice with small quantities of the fine cupric oxide, the washings (B) being poured into the tube similarly. The length of the mixture and fine cupric oxide should be about 10 cm. and over this a plug of ignited asbestos 1 cm. long is pushed in. The oxidised copper spiral (7 cm.) is now placed in position and at the exit end the reduced copper spiral is pushed in so as to touch the asbestos plug next to the coarse copper oxide. The tube is tapped gently so as to form a little channel above the layer of copper oxide and placed in the iron trough on the furnace. The exit end is connected to the Schiff's nitrometer (4), while the carbon dioxide generator is connected to the other end.

The nitrometer consists of a graduated burette  $A_1$  fixed to a heavy base and provided with an accurately ground stop-cock lubricated with vaseline or some stop-cock grease. The nozzle of the burette terminates in a funnel. The burette near its closed end and below the graduated portion has a side tube (*a*) fused to it, which is connected by rubber tubing to a levelling bulb (*c*) which rests on a ring (*d*) clamped to the burette itself and capable of sliding over it. A second side-tube (*b*) fused to the burette somewhat lower than the first is inclined upwards and resembles a V with a longer arm on one side, the bore of the tube being of capillary dimensions. This is connected to the combustion tube

preferably by a tube with a stop-cock in the middle. Mercury is poured into the azotometer till it rises about 1 cm. above the joint *b* and thus prevents the alkali solution entering the combustion tube.

When not in use the tube *b* is closed with pressure tubing and a screw-clip. The nitrometer is filled with a cold solution of two parts of potassium hydroxide dissolved in three to four parts of water with the addition of a trace of powdered barium hydroxide to prevent frothing.

**Combustion.** The apparatus having been connected up as shown (Fig. 56), the levelling bulb is lowered so as to transfer as much of the potash solution as possible into it and the sodium bicarbonate is heated so as to drive out all air. After about fifteen minutes, the burners under the reduced copper spiral and the layer of coarse copper oxide to within 12 cm. of the fine copper oxide, are heated so as to expel any occluded gases. After another fifteen minutes the stream of carbon dioxide is diminished by adjusting the heating of the bicarbonate and the azotometer is completely filled with potash by raising the levelling bulb and closing the tap. The bubbles should decrease in size as they ascend and finally disappear as specks near the top. When no appreciable volume collects near the top within about five minutes, the combustion of the substance may be commenced. The levelling bulb is raised, the tap of the azotometer opened, the collected gas if any is expelled and the tap closed after which the levelling bulb is lowered down as far as possible. The oxidised copper gauze is heated by lighting up the burners below it and the heating is extended slowly over the zone of fine copper oxide and the mixture, the heating being regulated so that not more than two bubbles of gas are ascending at the same time. The heating of the sodium bicarbonate should be *practically* stopped at this stage. The success of the analysis depends upon the gradual heating of the substance for which the burners should be lighted slowly one after the other, and the corresponding clay tiles covering the combustion tube laid on gradually. When the entire combustion tube has been raised to a dull red-heat and no more bubbles of nitrogen collect, the sodium bicarbonate is once again heated so that a moderate stream of carbon dioxide passes through the apparatus and drives out all the nitrogen into the nitrometer. The operation requires about fifteen minutes, the same precautions regarding the rise of

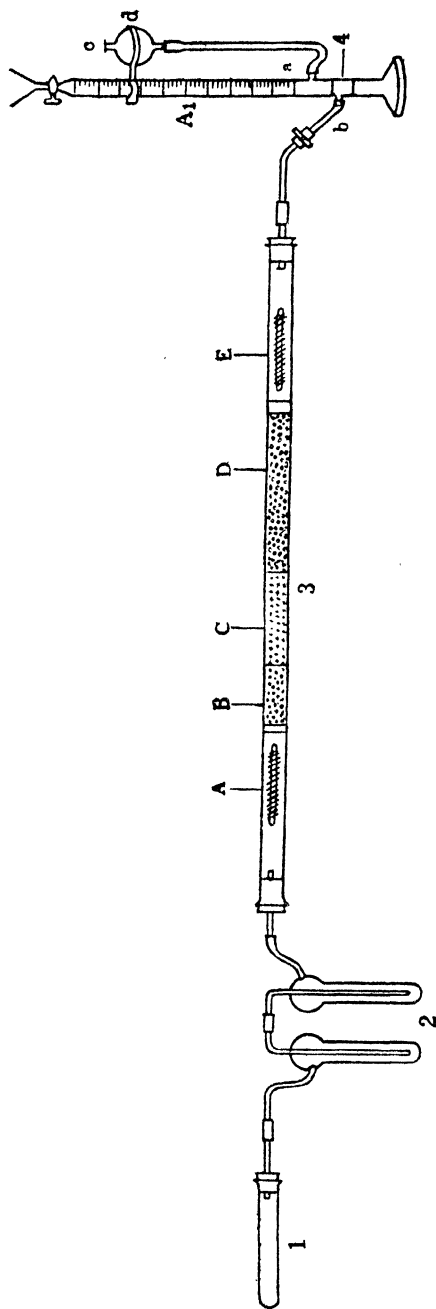


Fig. 56. Combustion tube connected up for determination of nitrogen.  
 (1) Bicarbonate tube. (2) Washing bottles. (3) Combustion tube filled. (4) Schiff's nitrometer.



bubbles being observed towards the end as were done during the preliminary heating. The azotometer is closed by the pinch cock and disconnected from the combustion apparatus at the rubber tubing. The burners under the spirals and the copper oxide are gradually turned down so that the tube gets cooled with a stream of carbon dioxide passing through, to prevent the reduced copper spiral from being oxidised. The levelling bulb is raised till the levels are equalised, the azotometer is removed away from the furnace, and a thermometer hung beside it. An hour later the volume of nitrogen is read off after equalising the levels, the temperature and the barometric pressure being noted at the same time.

### Calculation

$$\text{Percentage of nitrogen} = \frac{100}{W} V(P - p) \frac{0.001256}{760 (1 + 0.003665 t)}$$

where  $W$  = weight of substance taken in grams ;

$P$  = atmospheric pressure.

$p$  = vapour pressure of potash solution (taken as zero if 50% potash is used) ;

$V$  = volume of nitrogen collected ;

$t$  = temperature in degrees centigrade ;

or

$$\text{Percentage of nitrogen} = \frac{V \times w}{10 \times W}$$

where  $W$  = weight in grams of substance taken ;

$w$  = weight of nitrogen in milligrams per c.c. under the observed conditions of temperature and pressure ;

$V$  = volume in c.c. of nitrogen.

### Estimation of Nitrogen by Kjeldahl's process

A large number of nitrogenous organic compounds when heated with concentrated sulphuric acid in the presence of a catalyst like mercuric sulphate, or even a drop of mercury or copper oxide, undergo decomposition in such a manner that the nitrogen is completely transformed into ammonium sulphate. The ammonia is liberated by alkali, absorbed in a known volume of standard acid and the excess of acid is determined by titration. From the amount of ammonia formed the percentage of nitrogen can be calculated.

**Limitations of the method.** The method is largely used in agricultural analyses of soils, fertilisers, foodstuffs, etc., and a number of organic compounds in which nitrogen is present in a non-oxidised condition. It is not applicable to compounds wherein nitrogen is directly combined with oxygen such as the nitro-, nitroso- compounds and other nitrogenous substances like the azo-, hydrazo-, and diazo- compounds.

**Procedure.** A pear-shaped Jena glass flask of capacity 850 c.c. with a long neck commonly known as the Kjeldahl flask is placed on a cork ring and a clean dry funnel with a short stem is placed on the mouth of the flask. 0.5 to 1 g. of the dry substance, depending on the probable nitrogen content is transferred from a weighing bottle so that the substance falls directly to the bottom of the flask. The weight of the substance taken having been accurately determined, 15-20 c.c. of fuming sulphuric acid (10% sulphur trioxide) are carefully added through the funnel

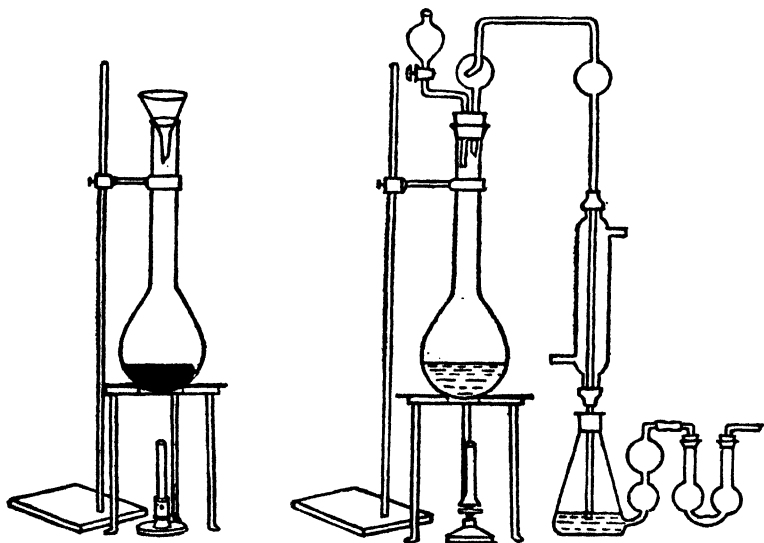


Fig. 57 A. Digestion flask.

Fig. 57 B. Ammonia distillation apparatus.

kept gently rotated, so as to transfer any particles sticking to the funnel into the flask which is also turned round so that the entire substance is wetted by the sulphuric acid. About 10 g. of potassium hydrogen sulphate or pure potassium sulphate (8 g.) are added to promote oxidation by raising the boiling point of the

acid. A small crystal of copper sulphate (0.1 g.) or a droplet of mercury or pure dried precipitated manganese dioxide (0.5 g.) the latter being added from time to time, assists the oxidation. The flask with the funnel replaced, is rested on a square piece of asbestos board with a central hole, placed over a tripod stand and clamped vertically in a retort stand (Fig. 57 A). The flask is heated gently at first and then strongly, the operation being conducted in a fume cupboard. The liquid darkens at first due to carbonisation and finally becomes clear and colourless or assumes a pale yellow colour in about 4 to 5 hours. Recently selenium has been used as the catalyst in conjunction with copper sulphate and mercuric oxide, the time for clearing being greatly reduced (20 to 30 minutes). 0.1 g. of selenium is used along with 0.1 to 0.2 g. of copper sulphate, 9 g. of potassium sulphate and 20 to 30 c.c. of concentrated sulphuric acid and the mixture heated for about 1 to  $1\frac{1}{2}$  hours after clearing. The flask is then cooled, the contents carefully diluted with water (40 c.c.) and finally made up to a known volume, say 250 c.c. 50 c.c. of this solution are pipetted into the digestion flask which is fitted with a two-holed stopper carrying a splash head or a trap tube and a bent dropping funnel and a piece of litmus paper is dropped into the flask along with pieces of washed porous porcelain (Fig. 57 B). The splash head is connected to a condenser, the inner tube of which dips into an absorption flask containing a known volume of standard sulphuric acid (30 to 40 c.c. of N/2 diluted if necessary). A strong solution of sodium hydroxide (40 g. of in 80 c.c. water) is placed in the dropping funnel and the alkali added drop by drop till there is an excess. The flask is then heated gradually till the contents boil gently and regularly and the distillation continued till nearly a third of the liquid had passed over. The absorption flask is now disconnected, the inner tube of the condenser as well as the part dipping into the acid, washed with distilled water and the excess of acid determined by titration with standard alkali (N/4) using methyl orange as indicator.

**Calculation.** Let  $w$  be the weight of the substance taken. Let  $V$  c.c. of acid expressed as normal be taken initially and  $V_1$  c.c. of alkali expressed as normal be required to neutralise the excess. Then

$$V - V_1 = \text{acid used for reacting with the ammonia.}$$

1 c.c. of N acid = .014 g. of nitrogen.

Hence percentage of nitrogen =  $\frac{(V - V_1) \cdot 014}{w} \times 100$ .

### Estimation of halogens

**Method of Carius.** This is a universal method applicable to all types of organic compounds and consists in oxidising the substance with fuming nitric acid in a sealed tube under pressure in the presence of silver nitrate crystals. The silver halide formed is then filtered and weighed.

**Requisites for the method.** (1) A thick walled soft glass tubing 50 cm. long and 15 to 16 m.m. diameter rounded off at one end, usually known as the Carius tube, thoroughly cleaned with chromic acid, washed with distilled water and dried.

(2) An ignition tube of 8 cm. length and 5-6 m.m. diameter to contain the substance.

(3) A thistle funnel with a long stem for introducing the nitric acid.

(4) Pure fuming nitric acid free from halogen. This may be tested by diluting 2 c.c. with about 20 c.c. of distilled water and adding a few drops of silver nitrate solution. The liquid should remain perfectly clear. Impure acid may be purified by distillation over silver nitrate, using a retort with a ground glass joint for the condenser.

(5) Pure silver nitrate crystals.

(6) Bomb furnace (Fig. 58).

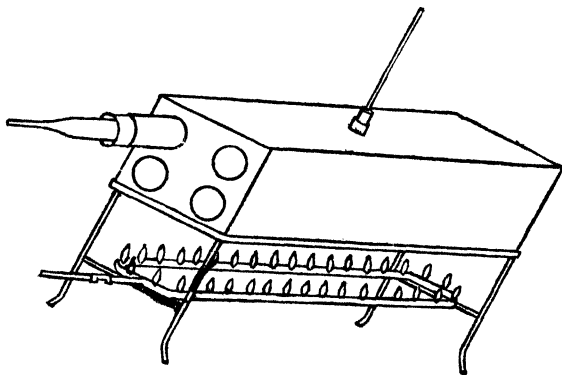


Fig. 58. Bomb furnace.

**Filling and sealing the tube.** About 0.2 to 0.3 g. of the finely powdered and dry substance is weighed accurately into the ignition tube which should be carefully wiped free from adhering particles before weighing. One gram of powdered silver nitrate crystals is introduced into the Carius tube through the thistle funnel followed by 2 c.c. of fuming nitric acid. The thistle funnel is removed without touching the sides of the tube. The tube is held slantwise and the ignition tube containing the substance is gently slipped in so that the substance does not come in contact with the acid. When the tube is held vertically, the open end of the ignition tube should be several centimetres higher than the level of the acid. If the substance is a liquid, it is introduced into a bulb with an open capillary, so that the capillary remains above the acid in the tube. The open end of the Carius tube is sealed in a blowpipe flame taking care that the substance does not come into contact with the acid at any stage.

When cold, the sealed tube is wrapped in asbestos paper with the drawn out capillary part projecting and placed in a protecting cylinder of iron and carefully introduced into the furnace which is always kept, for risks of explosion, in a special chamber provided with thick glass windows to observe the temperature. A luminous gas flame is also generally provided in the furnace chamber so as to help in the reading of the thermometer. The burner is lighted and the temperature raised very gradually and kept within 150-200° for about three to four hours and then at 250° for another two to three hours. The experiment is best commenced in the morning and completed by the evening, the tube being allowed to cool overnight.

**Opening of the sealed tube.** The tube which has been originally placed so that the capillary part projects out of the iron casing by about 4 cm. is warmed carefully in the Bunsen flame to drive the condensed liquid into the tube and the point is heated until the glass softens, when the pressure of the gases inside perforates the glass and nitrous fumes are evolved. *On no account* should the tube be removed from the furnace before this operation is concluded. Without removing the tube from the iron casing, a deep file mark is made 3 cm. below the capillary end and by touching the scratch with the pointed end of a red hot glass rod a crack is produced by leading which the top of the tube can be detached readily. Bits of glass, if any, adhering to the sides near the open

end are carefully removed. The contents of the tube containing the silver halide are now diluted by adding a few c.c. of water at a time and then washed completely into a beaker. The mixture is heated to boiling and the silver halide is filtered into a weighed sintered glass crucible (G 4), washed with hot water containing a little nitric acid till free from silver nitrate, dried at 140-150° and weighed.

### Calculation.

Percentage of halogen

$$= \frac{100 \times \text{At. wt. of halogen} \times \text{wt. of silver halide}}{\text{wt. of substance taken} \times \text{molecular wt. of silver halide}}$$

**Estimation of halogens by the method of Baubigny and Chavanne.** The apparatus to be used is shown in Fig. 59 and consists principally of the reaction flask V with a capacity of about 100 c.c. The flask has a ground-glass cap somewhat like that of a gas washing bottle, with an inlet tube (M, N) reaching to the bottom of the flask and an outlet carrying a number of absorption bulbs A, B, C, D, E. The absorption bulbs are filled through the opening O with nearly 30 c.c. of alkaline sodium sulphite (made by mixing equal parts of cold saturated sodium sulphite and 15% caustic soda solution). The end of the inlet tube M is closed with a rubber tube and glass plug; the ground joint is lifted up and the oxidising solution prepared in the flask itself as follows. 40 c.c. of concentrated sulphuric acid (sp. gr. 1.84) are introduced first, and then 1.15 g. of powdered silver nitrate and the mixture warmed till solution is complete. 4-8 g. of pure powdered potassium dichromate are immediately added and the whole warmed and shaken till the liquid becomes clear. The oxidation mixture is cooled and a small tube containing a weighed amount of the substance (.3 to .4 g.) is gently slid into the flask, and the neck immediately fitted to the ground glass joint which has been previously wetted with a drop of concentrated sulphuric acid to form an air-tight seal. Most of the organic substances are decomposed at the ordinary temperature, a little warming being necessary only at the end in order to ensure complete decomposition. With some substances, the reaction begins only on warming. The oxida-

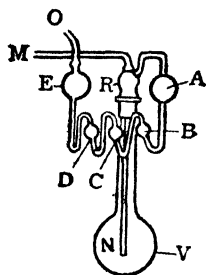


Fig. 59. Apparatus of Baubigny & Chavanne for halogen estimation.

tion should be carried out very cautiously so that no halogen escapes absorption in the sodium sulphite solution. If the reaction is too vigorous, it has to be moderated by cooling in water. The decomposition is completed, in most cases, in 30-40 minutes. For warming the flask, it is best to suspend it by a wire wound round the neck into a paraffin bath maintained at a temperature of 135-140°. The end of the reaction can be followed by the fact that no more gas evolution takes place. A fairly rapid stream of air is aspirated into the apparatus by connecting the tube O to the pump to drive out the last trace of chlorine or bromine into the absorption vessel. The apparatus is then disconnected, the end of the inlet tube is washed and the whole absorption system is placed in a tall beaker, so that the rim of the beaker is flush with the part R. By blowing strongly through O the liquid in the absorption vessel is transferred to the beaker and the whole washed with 30-40 c.c. of water three or four times.

The solution is treated with a considerable amount of nitric acid, heated till all sulphur dioxide is expelled, precipitated with silver nitrate, and the solution heated to coagulate the precipitate which is then filtered into a weighed glass crucible with sintered septum as in the previous experiment. The calculations are exactly the same.

**Estimation of sulphur in organic compounds.** The general method for the estimation of sulphur consists in oxidising it to sulphuric acid and subsequently precipitating it as barium sulphate. There are two methods in use, namely, (1) Carius method wherein the oxidation is effected by the use of fuming nitric acid, and (2) alkaline fusion in the presence of sodium peroxide.

**Carius method.** The procedure is identical with that described for the estimation of halogen except that neither silver nitrate nor barium chloride is placed in the Carius tube. About 0.2 g. of the substance is used and digested with 2 c.c. of fuming nitric acid (sp. gr. 1.50) with the addition of two or three crystals of potassium bromide. After heating in the furnace the bomb tube is cooled and opened as before and the contents washed into a beaker and filtered free from fragments of glass. The filtrate is diluted to about 300 c.c. with water, heated to boiling and precipitated with barium chloride solution, a large excess of the latte

being avoided. The liquid is heated over a small flame for about 1-2 hours till the precipitate settles and the supernatant liquid is clear. The precipitate of barium sulphate is filtered and weighed as usual.

**Fusion method.** About 0.2 g. of the substance is placed in a nickel crucible and intimately mixed with 5 g. of the fusion mixture made from 2 parts of anhydrous sodium carbonate and 1 of pure sodium peroxide, by means of a platinum wire. The whole is then covered with a deep layer of the fusion mixture.

The crucible is first heated very cautiously with a small flame which does not touch the crucible. The temperature is then gradually raised till the mass fuses to a clear liquid and effervescence has ceased. The mass is allowed to cool and dissolved in distilled water, the crucible being heated in the solution with the addition of a little bromine to oxidise any nickel sulphide formed. The hot solution is filtered, acidified with excess of hydrochloric acid and then treated with barium chloride solution to precipitate the sulphur as barium sulphate.

This method is particularly useful when both halogen and sulphur are present but it cannot be applied to easily volatile compounds. If the halogen also is to be estimated the melt is dissolved in water and acidified with nitric acid. Excess of silver nitrate is added and the silver halide filtered off and weighed. The filtrate and washings are treated with enough hydrochloric acid to precipitate the excess of silver as chloride, which is filtered off and washed. From this second filtrate and washings the sulphur present as sulphuric acid is precipitated with barium chloride and weighed as barium sulphate.

$$\%S = \frac{\text{wt. of BaSO}_4 \times 32 \times 100}{233 \times \text{wt. of substance taken}}.$$

### **Semi-micro method for the determination of carbon and hydrogen by combustion**

The micro-combustion of carbon and hydrogen was developed by Pregl in connection with the combustion of certain reaction products which were obtained in very small quantities insufficient for a macro-combustion. The method has been perfected by him in such a manner that a combustion can be carried out with great accuracy and in a short time with quantities of material from



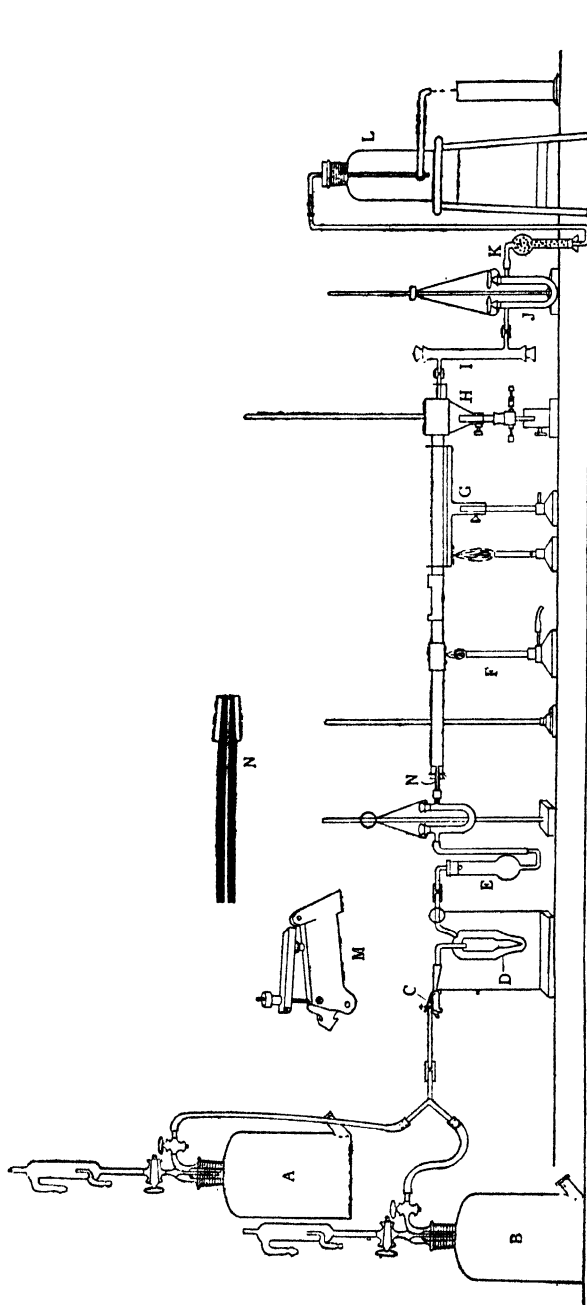


Fig. 60.

Bobrinski and Sucharda's apparatus for the semi-micro determination of carbon and hydrogen.

Gas holder for air.

E. Drying train.

F. Movable burner.

G. Tube burner.

H. Heating mortar.

I. Calcium chloride absorption tube.

J. Ascarite absorption tube.

K. Guard tube containing calcium chloride

L. Mariotte flask.

M. Precision pinchcock (Magnified).

N. Capillary connecting piece (Do.).

2 to 5 milligrams. The semi-micro method was attempted simultaneously by Dubsky and others with equal success. A micro-balance is unnecessary, an ordinary analytical balance (Paul Bunge's provided with a microscope scale) by which weighings up to  $1/100$ th of a milligram can be made, being quite efficient. The method enables the estimation to be made with 15 to 30 milligrams of solid and liquid substances and is characterised by a rapidity not readily attainable in ordinary combustions. The combustion tube when once filled can be employed for nearly twenty combustions. The duration of a single combustion from the time of introduction of the boat with the weighed material is nearly two hours and the limit of accuracy is about 0.2 per cent.

The apparatus described is the one employed by Bobranski and Sucharda for the centigram analysis of carbon and hydrogen, slightly modified as shown in Fig. 60.

**Apparatus and materials.** (1) Two gas holders, one for oxygen and the other for air, of capacity 2 to 3 litres, with a constant pressure-head and overflow, connected by a Y-tube to a pressure-regulator and a bubbler through a precision pinch cock shown separately in Fig. 60, (M).

(2) The pressure and speed of gases passing through the tube are of the greatest importance and the success of a determination largely depends on the constancy of pressure and speed during the heating. The pressure-regulator (Fig. 61) is very simple in construction and by raising or lowering the bell-shaped inlet and outlet tube fused in one piece, a pressure of 6-10 cm. of water can be maintained with the result that the gas speed is 3-5 c.c. per minute. The pressure-regulator may be dispensed with in a semi-micro combustion and the speed can be regulated by means of the precision pinch cock and the choking plug in the combustion tube itself. The Mariotte flask (aspirator bottle) at the other end further controls the pressure.

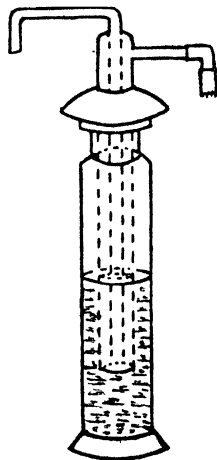


Fig. 61. A Pressure regulator.

**Purifying apparatus.** The drying train consists of an

ordinary straight calcium chloride tube (E) filled with calcium chloride connected to a small U-tube one limb of which contains ascarite and the other calcium chloride both separated by a plug of cotton wool. Above the layers of ascarite and calcium chloride are plugs of cotton wool pressed down by the stoppers.

**Combustion tube.** The combustion tube is made of Jena supremax glass about 50 cm. in length and with a diameter of 9.5 mm. to 10 mm. A neck of about 20-25 mm. length and 3 mm. outer diameter is fused at one of its ends. The bore of the neck should not be too narrow as otherwise it is likely to be choked by condensed water. A flattened silver wire (1 mm. thick) can be advantageously placed in the narrow path to prevent condensation of water.

**Combustion furnace.** The combustion tube is partly heated by a tube burner and partly by the heating mortar. The tube burner is about 25 cm. long and carries two V-shaped notches to support the combustion tube on which a brass collar slightly longer than the burner itself is slipped. The tube is therefore not heated directly and the metal collar prevents to some extent the bending of the tube.

**Heating mortar.** This is a hollow cylinder 65 mm. long and about 30 mm. external diameter surrounding a central metal chamber about 11 mm. bore to hold the combustion tube of which the narrow part alone, passes out through the mortar. A glass air-condenser is fixed by means of a screw-fitting to the mortar to condense the liquid used for heating and the mortar is heated from below by a micro-burner with an adjustable flame. A bent copper wire inserted into a hollow in the mortar prevents condensation of moisture in the narrow capillary of the combustion tube and drives it on to the calcium chloride absorption tube. The capacity of this is about 40 c.c. It is enough if 20 c.c. of dry dekalin or p-cymene is let into it by a pipette.

(*Note.*—The resin deposited after use of the dekalin for some time can be removed by pyridine bases admixed with some benzene).

**Absorption tubes : For water.** A Blumer's absorption tube (I) is used. This is filled with granular calcium chloride and plugged at both ends with cotton below the stoppers. The stoppers should be carefully vaselined so that when the tube is wiped before weighing, the vaseline is not removed. To avoid

this danger improved Flaschenträger tubes are being used. Before use 100 c.c. of carbon dioxide should be aspirated through it in the direction in which the gas will pass through during combustion and this should be finally displaced by passing 100 c.c. of dry air. A file mark is made on one of the connecting tubes and this end should always be connected to the ascarite tube.

**For carbon dioxide : Ascarite tube.** An ordinary U-tube (J) (10 cm. in length and 12 mm. bore) with ground stoppers is first cleaned and dried. A plug of cotton is pushed in one limb to a depth of about 3-4 cm. below the stop-cock. The space above is filled with granular calcium chloride over which another plug of cotton is placed and the stopper lightly smeared with vaseline is inserted. Care should be taken that the vaseline is not pushed out to such an extent as to be mechanically removed during the wiping of the tube before weighing. The rest of the tube is filled with ascarite and then another wad of cotton-wool is pushed in after which the stopper is replaced. Ascarite is capable of absorbing ten times as much carbon dioxide as soda-lime and by using it, the stage at which the tube has to be refilled is easily recognised since the portion which has absorbed carbon dioxide becomes perfectly white. The disadvantage lies in the difficulty of removing the exhausted filling which adheres to the glass as a very hard compact mass. A mixture of equal quantities of soda-lime and ascarite is therefore recommended sometimes.

Immediately after the absorption train a calcium chloride tube filled with calcium chloride is attached by a long glass tube to the aspirator bottle usually called the Mariotte flask. The calcium chloride used should previously be ignited so as not to fuse and this same calcium chloride should be used for all the fillings.

When not in use the long glass tube connected to the aspirator and the calcium chloride tube of the purifying train should be connected up to keep the combustion tube dry.

**Mariotte flask.** This is an aspirator bottle of about 600 c.c. capacity with an outlet at the bottom, supported on an iron tripod stand. The neck of the bottle carries a one-holed stopper through which a quill tube bent twice at right angles is pushed in to reach nearly the bottom. The outlet also carries a one-holed cork fitted with a bent-tube nearly of an S shape. This serves to maintain an adjustable and definite reduced pressure in the system.

**Materials. Oxygen.** The gas is prepared by heating a mixture of potassium chlorate and manganese dioxide very slowly and collecting the gas in an air-tight Pepys gas holder from which it may be transferred to the glass gasholder of the combustion outfit. Compressed oxygen from a steel cylinder may also be used.

**Air.** The air from the open is preferable to the laboratory air which is usually contaminated with vapours of organic solvents.

**Rubber connections.** Impregnated rubber tubing should be used for connecting the absorption tubes to each other and to the combustion tube. For other connections good cloth-lined rubber tubing may be used.

**Asbestos.** Good gooch asbestos purified as usual and strongly ignited in a porcelain basin before use is sufficient.

**Platinised asbestos,** should be so pure as to be capable of igniting a jet of hydrogen.

**Silver wool.** This is really fine wire which has to be cut up into small pieces or coiled and pushed into the tube. Before use it has to be ignited in a current of hydrogen and then in a current of oxygen. Instead of this silver asbestos may be substituted. It may be made by mixing together finely divided silver (*see* Appendix) with moistened gooch asbestos and igniting.

**Lead chromate—copper oxide.** Pure wire form copper oxide coated with pure precipitated lead chromate so as to form a layer of 1 mm. thickness can be used. This is available in the market but should be ignited strongly before use as some specimens have been found to give off oxides of nitrogen.

Alternatively, pieces of purified pumice 2-3 mm. in size are coated with a paste made by a mixture of equal parts of finely powdered wire-form cupric oxide and precipitated lead chromate so as to form a layer of 1 mm. thickness. This is then dried in the steam oven and ignited in a clean porcelain basin over a Techlu burner.

**Lead peroxide.** Either granulated peroxide or lead-peroxide asbestos can be used, but the former is preferable as the filling can be used for a longer period.

**Liquid for heating mortar.** Dekalin is distilled and stored in a bottle over anhydrous calcium chloride. *p*-cymene may also be used.

[Pieces of flannel and soft chamois leather are washed with soap and finally with distilled water, dried in shade and preserved in stoppered specimen jars for protection from dust.]

**Filling the combustion tube.** The combustion tube is plugged at the narrow end, filled with hot chromic acid-sulphuric acid mixture and kept overnight after which it is thoroughly washed first with tap water and then with distilled water. The tube is then air dried or it may be rinsed with a few c.c. of alcohol. The alcohol is removed by a current of hot air and the tube heated to its entire length on the blast lamp. When cold the tube is next filled as detailed below commencing from the neck-end which goes into the heating mortar. The filling called Pregl's "universal filling" is suitable for all types of compounds including those containing nitrogen, sulphur and halogens. Lead peroxide is the best absorbent for oxides of nitrogen, silver wool or silver-asbestos for halogens, lead chromate for sulphur oxides and copper oxide is the oxidising agent. Lead peroxide unfortunately retains moisture, and a constant moisture condition is maintained by the heating mortar.

The details of filling are as follows :

- |                                            |   |                                                   |
|--------------------------------------------|---|---------------------------------------------------|
| (1) Asbestos 2-3 mm.                       | } | Portion of filling covered by the heating mortar. |
| (2) Silver wool 13 mm.                     |   |                                                   |
| (3) Asbestos 2 mm.                         |   |                                                   |
| (4) Lead peroxide 30-35 mm. or more        |   |                                                   |
| (5) Platinised asbestos 8-9 mm.            |   | Choking plug.                                     |
| (6) Silver wool 37 mm.                     |   |                                                   |
| (7) Asbestos 2 mm.                         |   |                                                   |
| (8) Copper oxide and lead chromate 175 mm. |   |                                                   |
| (9) Asbestos 2 mm.                         |   |                                                   |
| (10) Silver wool 35 mm.                    |   |                                                   |
| (11) Asbestos 2 mm.                        |   |                                                   |

The length of the unfilled portion is about 190 mm. and this is beyond the tube burner. The cleaned tube is first filled in the order indicated above up to the choking plug. The lead peroxide dust adhering to the inner surface of the tube is removed by wiping with a plug of cotton wool attached to a wire or a glass rod. The platinised asbestos is then introduced and is pressed gently with a flattened glass rod. The filling is stopped at this stage and the tube fitted up with a tight-fitting stopper carrying a short piece of capillary tubing drawn out slightly. A slight smear of glycerine

facilitates the introduction of the stopper. The tube is connected up as shown (Fig. 59) and the apparatus tested to see if the necessary friction has been introduced by the choking plug, by sending in a stream of air so that the bubble frequency is 70-80 per minute and 3 to 5 c.c. of water collect in the measuring cylinder below the Mariotte flask. If the speed is greater the choking plug must be gently compressed or if it is less, the compression has been too much. After this test, the rest of the filling is completed as outlined.

**Blank test.** Before a regular combustion can be begun, the combustion tube must be preheated and the lead-peroxide portion of the filling brought to a constant moisture condition as on this alone the correct percentage of hydrogen depends. The absorption tubes are disconnected and the combustion tube connected up with the rest of the apparatus. Ten to fifteen c.c. of dekaline are introduced into the heating mortar, the micro-burner below is lighted up and the size of the flame adjusted so that the dekaline refluxes steadily. The stopper with the short piece of capillary tubing is removed from the combustion tube, the tube burner below the filling is lighted up and the unfilled portion of the tube is heated along its entire length by a movable burner F for about ten minutes, to burn away any organic matter. After the tube has cooled, the rubber stopper is replaced and the filling heated for a period of about 6 hours in a stream of dry air passing through at a slightly faster rate than the one indicated already. After this preliminary heating, the weighed absorption tubes have to be connected up to the combustion tube and 100 c.c. of dry air aspirated through the apparatus, after which the tubes are disconnected and weighed. This process has to be repeated till the absorption tubes show no change in weight or do not differ in weight by more than 0.02 of a milligram. When this stage is reached the apparatus is ready for a combustion.

**Preparing the material for analysis.** With low-melting solids, drying for twenty four hours in a vacuum desiccator may be sufficient while with solids having higher melting points the drying pistol with a suitable bath liquid may be used.

**Carrying out an analysis.** The doors of the balance case are opened so as to enable the balance to attain the temperature of the surroundings. Meanwhile the burners below the heating mortar, and the filling are lighted up, the rubber stopper with the capillary is removed and the open end of the combustion tube

is wiped with a wad of cotton. The siphon in the Mariotte flask is adjusted so that a current of air is aspirating through the combustion tube. The entire unfilled portion of the tube is now heated with a movable burner and the short brass collar, beginning from the open end onwards. When the open end has cooled, the stopper with the capillary is re-inserted and the rate of flow of gas is adjusted to a bubble frequency of 4 c.c. per minute, and 100 c.c. of air aspirated through the apparatus from which the absorption tubes have been disconnected already. Meanwhile the absorption tubes are weighed observing the usual precautions. The platinum or porcelain boat which has been cleaned by boiling with dilute nitric acid, washed with water, flamed and kept on the weighing block in a desiccator is placed on the balance pan by means of forceps and is weighed after a few minutes. About 15 mg. of the dry material (not exceeding 25 mg.) are introduced into the boat by a small clean nickel micro-spatula and pressed down lightly. Holding the hook of the boat by the forceps any material adhering to the outer surface of the boat is removed by wiping with a small camel-hair brush and the boat with the substance is weighed once again, after which it is placed on the metal block in the desiccator. If the material is hygroscopic the boat is introduced into a weighing tube without the substance and the combination weighed. After the introduction of the substance the combination is weighed again.

The  $\text{CaCl}_2$  absorption tube is connected to the ascarite tube by impregnated rubber tubing and the former is connected to the combustion tube while the latter is connected to the Mariotte flask through the guard tube (calcium chloride). The joints in all these cases should be glass to glass.

The rubber stopper of the combustion tube is removed and the boat containing the weighed substance is introduced by means of forceps and pushed in by means of a glass rod to about 30 mm. from the filling. The stopper is replaced and pushed as far as possible, oxygen is turned on instead of air, and the apparatus is tested for air-tightness. The longer brass collar is pushed over the boat while the shorter one is placed a few cm. away from the burner and is nearly midway between the stopper and the boat. As the size of the flame in the tube burner gets smaller near the ends the portion of the filling covered by the brass collar and nearer the boat is heated by an additional burner. With the rate of oxygen



adjusted to the usual bubble frequency, the heating with the movable burner is commenced beginning from the short-brass collar and proceeded with slowly. After about fifteen minutes the substance might melt and sublime sometimes or carbonise slowly. When carbonisation is complete the movement of the burner may be done more rapidly. Heating generally lowers the bubble frequency which however returns to its normal value after a time. This will also be the case each time the brass collar is moved. Sometimes, substances form a difficultly combustible graphitic carbon. In such cases, the boat is cooled for a time after the first ignition and re-heated. When the burner has been moved up to very near the tube burner and the material has been fully burnt, the burner is moved back to the original point at which heating was commenced and the oxygen is replaced by air with the measuring jar kept below the siphon from the Mariotte flask. Dry air (100 c.c.) is aspirated to displace any carbon dioxide remaining in the calcium chloride tube and combustion tube and to restore the initial conditions. During the heating the copper wire of the heating mortar is slipped over the neck of the combustion tube to prevent any condensation of moisture there. Any moisture in the side tube of the calcium chloride tube is driven into the tube by placing a heated micro nickel spatula on it from time to time. The final aspiration of air takes from 20 to 25 minutes. To disconnect the absorption tubes, the siphon tube from the aspirator is raised upwards, the stop-cocks of the absorption tubes are closed, and the absorption train disconnected. The calcium chloride tube attached to the Mariotte flask is connected to the combustion tube and if a second combustion is to be done the aspiration of air is continued till it is to be begun. Otherwise the burners are put out and the long glass tube connected with the Mariotte flask is connected up to the drying and purifying trains so that the combustion tube is dry when not in use.

**Wiping and weighing of the tubes after analysis.** Immediately after disconnecting the tubes, they are placed on the stand, removed to the balance room and left to cool for about fifteen minutes. Then any fragments of rubber tubing or dirt in the connecting pieces of the absorption tubes are removed by a tuft of cotton wad attached to a nickel wire. This should be done with care so as not to remove any vaseline. A piece of moistened flannel is held in each hand and the surfaces of the tubes are wiped

with these by a rotatory motion beginning from the middle and proceeding to the end. The wiping is then repeated with the chamois leather. The absorption tubes are placed on the stand, taken near the balance and kept for about ten minutes. The calcium chloride tube is placed first on the pan and weighed after five minutes. The ascarite tube is then weighed immediately. In general the weighing should be done twenty minutes after the wiping.

In carrying out weighings with a sensitive balance up to  $1/100$ th of a milligram, it is convenient to record deflections with the middle point of the microscope scale as zero. For example a deflection of 2.5 scale divisions to the right is regarded as 25 right while 3 divisions to the left as 30 left. The mean deflection from the zero point is 5 left which means that .05 m.g. has to be deducted from the weights on the pan and that indicated by the rider. A mean deflection to the right indicates that an addition has to be made to the indicated weight.

**Automatic regulation of combustion.** In Pregl's method the rate of combustion of a substance is controlled by adjusting

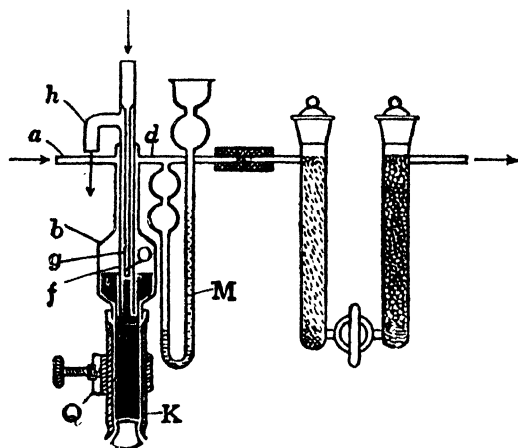


Fig. 62. Automatic regulator for combustion.

the oxygen bubble frequency by means of a precision pinch-cock. When it is not possible to watch the progress of the combustion from start to finish, recourse may be had to the automatic regulating device of Bobranski and Sucharda, which acts by controlling the rate of vaporisation of the substance combusted,

while ensuring a continuous and constant supply of an excess of oxygen. The apparatus (Fig. 62) is a manometer and a thermo-regulator combined and used as such ordinarily. When it is not desired to use the thermo-regulator which automatically controls the combustion, the manometer alone can be used.

The apparatus is cleaned with chromic acid mixture, dried, fitted with the rubber tubing K, closed at the open end with a small piece of glass rod and the screw pinch-cock Q slipped over the rubber tube. The manometer is filled with potassium carbonate solution coloured by a trace of solid phenolphthalein. The apparatus is interposed between the precision-pinch-cock and the purification train. Mercury is poured through the gas inlet tube *g*, the end O of which is cut off at an angle of 30° and closed by means of a sintered glass plate, till it is within 3-4 mm. of the end O. The gas outlet *h* is connected to a small burner used to vapourise the substance. The precision-pinch-cock is now closed completely and the tap of the oxygen gas holder opened fully. The precision pinch-cock is opened carefully till the manometer shows a rise of 6 cm. That the requisite amount of mercury has been introduced can be tested by unscrewing the pinch-cock Q on the rubber tube completely, lighting up the burner and then screwing in completely the pinch-cock. The flame which should be 5 cm. higher should be extinguished. If this does not happen, more mercury should be added. The small burner is placed just below the ear of the platinum boat containing the substance to be combusted, this part of the combustion tube being surrounded by the movable brass collar. During the combustion, the substance volatilises, part of the vapour being carried along by the oxygen stream, while the remainder condenses on the cooler upper part of the combustion tube. Back volatilisation of the substance and the products of combustion is prevented by heating the combustion tube in front of the boat to a dull red heat with another burner. When the pressure becomes high due to rapid combustion, the gases or vapours formed depress the mercury in the outer tube, which rising in *f* cuts off the gas supply by closing the end O. The flame originally 5 cm. high gradually diminishes in size and is extinguished completely when the pressure reaches 15-20 mm. and burns at the auxiliary jet of the burner. When the pressure drops down, the mercury recedes, gases pass through the burner which gets

lighted up, gradually reaching to its full length. Thus the combustion gets controlled chiefly through the variations of pressure produced by the products of combustion. (Sucharda and Bobranski).

## DETERMINATION OF NITROGEN

### Semi-micro combustion

The general principle of the method is the same as that of Dumas for the micro-method. The apparatus and accessories required are outlined below.

(1) The combustion tube is similar in size to that employed for carbon and hydrogen and when larger quantities, say, 15 to 20 milligrams, are employed, the diameter of the tube may be increased to 11 mm. (internal), the length remaining the same.

(2) **CO<sub>2</sub> supply.** The accuracy of the method depends largely on the purity of the carbon dioxide used. With a little precaution the gas of the necessary purity may be obtained readily and quickly from the Kipp itself. The marble used may be boiled in water, each piece etched with dilute hydrochloric acid and washed with water before charging into the Kipp. The pure concentrated hydrochloric acid used may be diluted with an equal volume of boiled water. The gas is drawn from the highest point in the middle bulb by means of a bent tube (Fig. 63). After charging the Kipp the tap is opened and a vigorous evolution of gas expels the air. This operation repeated twice or thrice ensures air-free gas. One or two pieces of marble put in so that they remain lodged in the stem, continuously generating the gas help in the deaeration of the liquid. This deaeration is advantageous even while the combustion is going on. The spent acid is not thrown away but utilised for diluting the fresh concentrated acid in the proportion of 1:1.

(3) **Azotometer.** The azotometer (Fig. 63, N) has a capacity of 8 c.c. with each small division amounting to 0.02 c.c. in the capillary part of the tube. The tube has a tap at the top ending in a funnel. The tap on the CO<sub>2</sub> inlet tube has a long lever arm which enables the gas speed to be correctly regulated. At the end of the bore, the plug of the stopper has two grooves, 4 mm. long, cut oppositely so as to make the adjustment of speed quite

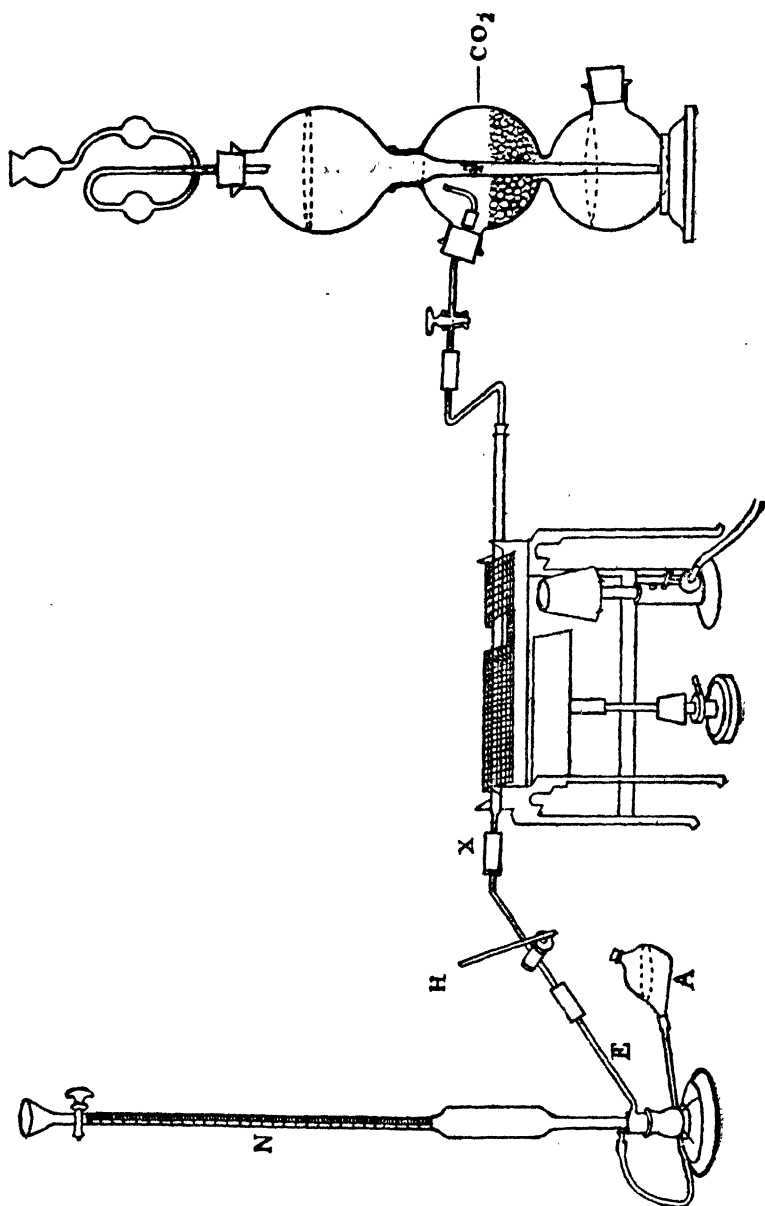


Fig. 63. Apparatus for semi-micro determination of nitrogen.

easy. A correction of 1.2% has to be applied to the volume read off to allow for the liquid sticking to the sides of the tube.

The azotometer is first cleaned by filling it with chromic acid mixture by keeping overnight. It is then washed with tap water and finally with distilled water and allowed to drain completely. The levelling tube is connected and the rubber connection bound with nickel wire so as not to slip when filled with alkali. Pure mercury is poured through the levelling tube till the level is midway between the side tube connecting the levelling bulb (A) and the tube E connecting with the stop-cock H. Sufficient alkali is added to fill the measuring tube and about a third of the levelling bulb. Sometimes air bubbles adhere tenaciously to the mercury surface and alkali. These disappear after a time when a sufficient amount of very fine copper oxide dust collects on the surface.

(4) **Weighing tube.** The weighing tube Fig. 64 from which the substance is weighed out is about 35 mm. in length with a width of 4 mm. at the open end and 2-3 mm. at the closed end. It has a stopper with a long handle (2) and an aluminium wire is coiled round the tube so as to form a supporting frame. If the

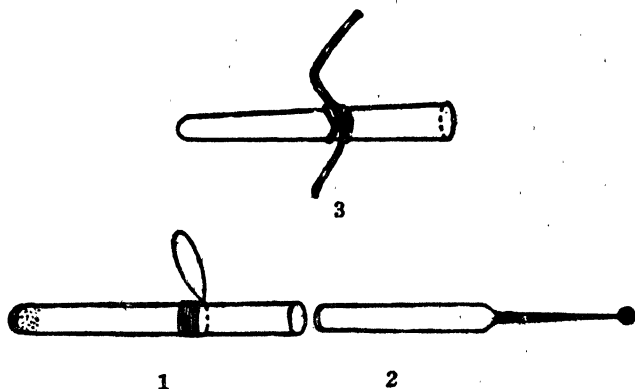


Fig. 64. Weighing tube.

substance is not hygroscopic, an ignition tube 40 mm. long and 5 mm. bore, Fig. 64 (3) can be used.

(5) **The mixing tube.** For mixing the substance with fine CuO a test tube (4 in.  $\times$   $\frac{1}{2}$  in.) provided with a cork or a mixing tube with a ground glass stopper can be used. A filling funnel drawn out from an ordinary test-tube at about its middle so that

the drawn-out portion is 5 mm. in diameter and 60 mm. long, is indispensable.

(6) **Non-frothing 50% KOH.** 200 g. of pure KOH pellets are dissolved in 200 c.c. of water and 5 g. of finely powdered baryta are added and the mixture shaken. The liquid is allowed to settle and then filtered through a dry Buchner funnel using an ordinary filter paper.

(7) **Copper oxide.**

Coarse : Pure wire form copper oxide ignited before use.

Fine : The wire form oxide is powdered, sieved and stored in a bottle.

Reduced copper : The combustion tube is packed with the wire form copper oxide and the latter is reduced in a current of hydrogen, cooled and transferred to a bottle while still warm.

The filling of the combustion tube. The combustion tube is filled, commencing from the narrow or drawn-out end, as detailed below :—

- (1) Silver asbestos to cover the conical part.
- (2) Asbestos 2 to 3 mm.
- (3) Wire form copper oxide 100 mm.
- (4) Reduced copper (from wire form oxide) 50 mm. Some use a roll of reduced copper gauze of the same length. } Permanent filling.
- (5) Asbestos 2 mm.
- (6) Wire form copper oxide 10 mm. (to be renewed after each analysis).
- (7) Fine copper oxide a few mm. in length followed by the mixture of oxide and the substance and finally fine copper oxide. The total length of this should be about 70-90 mm.
- (8) Coarse wire form copper oxide, 50 mm. When a boat is used a roll of oxidised copper gauze is substituted.

After the combustion tube has been filled with the permanent filling, the tube is placed on the stand, connected up as in Fig. 21 and the filling heated in a current of carbon dioxide under a slight pressure. The heating should be commenced only after micro-bubbles (less than 0.2 mm. diameter and about 0.004 c.mm. or 1/5 of the distance between the small divisions) are seen to appear

in the nitrometer. While the permanent filling is getting preheated the weighing and mixing of the substance can be proceeded with.

**Weighing and mixing.** The weighing tube with the substance is weighed first and holding the dry mixing tube on the left hand, from 10 up to a maximum of 20 milligrams of the substance are transferred to the mixing tube so that the particles fall



Fig. 65. Filling funnel.

directly to the bottom of the tube. The weighing tube is replaced on the balance and weighed after sometime. The material covered with fine copper oxide, 3 to 4 cm. depth, the tube corked and then mixed by shaking. The combustion tube is cooled and when quite cold, is detached and the funnel (Fig. 65) is inserted into the combustion tube. The mixture of copper oxide and material to be analysed is poured in from the mixing tube with gentle rotation and tapping. The mixing tube is washed with fine copper oxide twice, with half the amount of copper oxide used originally, corking the tube each time, shaking well and pouring into the combustion tube. The rest of the filling is completed afterwards.

**Course of the analysis.** The tube with the completed filling is placed on the combustion stand so that about 2-3 cm. of the filled portion at the narrow end projects beyond. The bigger wire-gauze roll (Fig. 63) is slipped over the permanent filling and the smaller roll is brought to the boundary between the empty part of the tube and the wire form copper oxide. The tube is connected up as in the figure and the tube burner is placed below the permanent filling. The azotometer is emptied so that the alkali is in the levelling bulb, the stop-cock H is opened fully and a stream of carbon dioxide passed while the permanent filling and the coarse copper oxide covered by the long roll of wire gauze is gradually heated to dull redness. After passing the gas for about two minutes, the liquid is forced into the azotometer, and the tap at the top is closed, the stop-cock H is adjusted to give a frequency of 2 bubbles per second and the size of the bubbles ascending the nitrometer is watched. If the bubbles are less than 0.2 mm. diameter and ascend very slowly up the tube, the passing of carbon dioxide is stopped. The stop-cock H is then opened carefully and the movable burner provided with a flame guard is placed at



the boundary between the empty tube and the copper oxide filling. At this stage a renewed evolution of gas stopping after some time, takes place. The upper cock of the azotometer is opened and the froth is expelled, a few c.c. of the potash allowed to rise in the funnel and the tap then closed. The movable burner is moved a few mm. forward and its shift is so manipulated that not more than 2 bubbles per 3 seconds pass up the azotometer. When the bubble frequency slackens the burner is moved slightly forwards. Ultimately when the substance has been heated fully the burner can be moved a little more rapidly and brought near the fixed burner. The movable burner can then be retraced and brought back alongside the fixed burner. The stop-cock H is closed fully and the stop-cock of the Kipp opened. The stop-cock H is opened gradually so that the bubble frequency (2 per 3 seconds) is maintained. During the initial stages of this scavenging the copper oxide layer of the permanent filling can be heated by an additional burner. Towards the end, when the bubbles gradually diminish in size, all the burners are extinguished. When the bubbles have reached the micro size, the levelling tube of the azotometer is raised to the top near the funnel and supported on the ring. The stop-cock H is closed and the azotometer detached at the point X from the combustion tube and removed to a cooler room, preferably near the barometer. A thermometer is suspended near the measuring tube, any froth collected is broken up by raising and lowering the levelling bulb carefully and tapping on the tube. After fifteen minutes the volume is read off. A deduction of 1.2% of the volume is made to allow for the liquid sticking to the sides. The calculation is made as usual.

## CHAPTER XII

### SOLVENTS AND REAGENTS

#### Preparation of pure solvents

**Absolute ethyl alcohol.** Ethyl alcohol of a high degree of purity is frequently required in the organic laboratory. It may conveniently be prepared by the dehydration of rectified spirit, which is the constant boiling point mixture which ethyl alcohol forms with water, usually containing about 95.6 per cent of alcohol by weight.

About 3 litres of rectified spirit are introduced into a 5 litre bolt-head flask and treated with freshly ignited (and cooled) quicklime. The flask is fitted with a double surface condenser carrying a calcium chloride guard tube at the top. After leaving over-night, the mixture is refluxed for eight hours and again left over-night. Next morning, the condenser is set for distillation and fitted with a receiver (a 3 litre Buchner flask) carrying a calcium chloride guard tube. It is advisable to employ rubber corks throughout. Heating is carried out by a water-bath. The alcohol obtained by this procedure may be about 99.5 per cent pure and is suitable for most purposes where absolute alcohol is required.

There are however some reactions in which anhydrous alcohol has to be employed and this may be made from the absolute alcohol by the following procedure. 7 g. of sodium are added to one litre of 'absolute' alcohol and 27.5 g. of pure ethyl phthalate are added after the sodium has reacted. The mixture is gently refluxed for 2 hours after which the alcohol is distilled using a short column. The first 25 c.c. of the distillate are rejected. All the operations have to be carried out with rigid exclusion of moisture, because of the extremely hygroscopic nature of alcohol. With proper precautions, it is possible to prepare ethyl alcohol containing less than .01 per cent of water by this procedure.

**Absolute methyl alcohol.** Commercial methyl alcohol may first be dehydrated by quicklime as in the case of ethyl alcohol. The product, which may be 99 per cent methyl alcohol may further be dehydrated by the following procedure. 5 g. of clean dry magnesium turnings and 0.5 g. of resublimed iodine are placed in a 2 litre

pyrex flask fitted with a double surface condenser. 50 c.c. of the methyl alcohol are added through the condenser and the mixture warmed on a water-bath until the iodine disappears. If a vigorous evolution of hydrogen does not set in a further 0.5 g. of iodine is added and the flask warmed until all the magnesium has been converted to the methoxide. 900 c.c. of the methyl alcohol are then added and the mixture boiled under reflux for 30 minutes. The product is then distilled with exclusion of moisture, the first 25 c.c. of the distillate being discarded.

If a small proportion of acetone is present in the methyl alcohol (less than 1%), it may be removed by the following procedure. A mixture of 500 c.c. of the methyl alcohol, 25 c.c. of furfural and 60 c.c. of 10% sodium hydroxide is refluxed in a 2 litre round-bottomed flask for 12 hours. The alcohol is then carefully fractionated through an efficient fractionating column. The first 25 c.c. are rejected. The methyl alcohol may then be dehydrated by the procedure described earlier.

**Absolute ether.** The chief impurities in commercial ether are water, ethyl alcohol and in samples which have been exposed to air and light for some time, 'ether peroxide.' Peroxides may be detected by shaking a small sample with an equal volume of 2% potassium iodide solution and a few drops of dilute hydrochloric acid. A brown colouration or blue colouration after addition of starch solution indicates the presence of peroxides. The peroxides may be removed by shaking with a concentrated solution of ferrous salt prepared by dissolving 60 g. of crystallised ferrous sulphate in 6 c.c. of concentrated sulphuric acid and 110 c.c. of water. 20 c.c. of this solution diluted to 100 c.c. with water may be employed for 1 litre of the ether. After this treatment, the ether is allowed to stand over 150 g. of anhydrous calcium chloride for 24 hours with occasional shaking. The water and the alcohol present are largely removed. The ether is then filtered through a large fluted filter paper into a dry bottle (all flames in the vicinity must be extinguished). Fine sodium wire is then directly introduced into the bottle by means of a sodium press (Fig. 67). If on the following day no bubbles of hydrogen rise from the surface of the sodium and the latter still possesses a shiny surface, the ether is ready for use. If the sodium is badly attacked, the ether is filtered into another dry bottle and treated with fresh sodium wire.

**Acetone.** Synthetic acetone of a high degree of purity is available from the Ordnance Factories in India. The water present (about 1%) may be removed by keeping the acetone over anhydrous calcium chloride for two days, filtering from the drying agent and distillation.

**Ethyl acetate.** Commercial ethyl acetate may be purified by washing with an equal volume of 5% sodium carbonate solution, then with saturated calcium chloride solution, drying over anhydrous potassium carbonate and distilling. Final drying may be accomplished over phosphorous pentoxide, after which the ethyl acetate is filtered and distilled with exclusion of moisture.

**Chloroform.** Commercial chloroform contains about 1% of ethyl alcohol, which is added as a stabiliser. This grade of chloroform cannot be used for chromatographic work. The alcohol may be removed by shaking the chloroform five or six times with about half its volume of water, drying over calcium chloride for 24 hours and distillation. The solvent when free from alcohol must be stored in a dark bottle to avoid the photochemical formation of phosgene.

**Benzene.** Commercial benzene contains thiophene as an impurity. Pure dry benzene may be prepared by the following procedure. The benzene is placed in a large separatory funnel fitted with a mechanical stirrer. 80 c.c. of concentrated sulphuric acid per litre of benzene are added and the mixture stirred vigorously. The sulphuric acid layer is tapped off and treatment with further quantities of sulphuric acid continued till the acid is practically colourless. The benzene is then distilled and the distillate dried by the addition of sodium wire.

**Toluene.** Toluene free from sulphur compounds may be prepared by treatment with sulphuric acid. Control of temperature is necessary since toluene is more readily sulphonated than benzene. One litre of commercial toluene is stirred with 100 c.c. of concentrated sulphuric acid for 30 minutes keeping the temperature below 30°. The acid layer is removed and the process repeated twice. The toluene may then be distilled and dried over sodium wire.

**Petroleum ether.** Refined petroleum with various boiling point ranges are commercially available. It is not advisable to employ any fraction with a boiling range of over 20°. Unsaturated

substances present may be removed by vigorous saking with 10% of the volume of concentrated sulphuric acid twice or thrice and then with a concentrated solution of potassium permanganate in 10% sulphuric acid until the colour of the permanganate is unchanged. The solvent is then washed with water, dried over calcium chloride and distilled. Final drying is achieved by leaving over sodium wire.

**Dioxan.** Commercial dioxan contains some acetaldehyde, glycol acetal and water. Purification is effected by refluxing 1 litre of the commercial dioxan with 14 c.c. of concentrated hydrochloric acid and 100 c.c. of water for 12 hours, while a slow stream of nitrogen is bubbled through the solution to remove the acetaldehyde formed. The cold solution is treated with potassium hydroxide pellets with shaking until some remain undissolved. The aqueous layer is separated and the dioxan is kept over fresh potassium hydroxide pellets for 24 hours. The dioxan is then refluxed over sodium until reaction ceases and part of the sodium remains bright. The dioxan is then distilled over sodium and stored out of contact with air.

**Tetrahydrofuran.** This is an excellent solvent for a wide variety of organic compounds. It has been frequently employed for carrying out reductions with lithium aluminium hydride in cases where the use of ether has not proved feasible. Commercial tetrahydrofuran is purified by keeping over potassium hydroxide pellets for two weeks, filtering, keeping over sodium for a week, followed by distillation over sodium and adding sodium wire to the distillate.

**Pyridine.** Pyridine of analytical reagent grade is dried by refluxing over potassium hydroxide pellets and distilling with careful exclusion of moisture.

### **Special reagents used in the organic laboratory :**

**Alcoholic potash.** (1) 10 g. of pure caustic potash in the form of pellets are dissolved in 10 c.c. of water and diluted with absolute alcohol to 400 c.c. The solution is agitated with 10 g. of anhydrous sodium sulphate till it becomes clear and then decanted. Or

(2) 15 g. of caustic potash are agitated with 500 c.c. of 95% alcohol at the ordinary temperature until solution is complete. After settling, the clear solution is decanted.

**Bromine in carbon tetrachloride.** 2 c.c. of liquid bromine are dissolved in 50 c.c. of dry carbon tetrachloride.

**Benedict's solution.** (Reagent for aliphatic aldehydes and reducing sugars). This solution is prepared by dissolving 17.3 g. of copper sulphate crystals in 100 c.c. of water and separately 173 g. of sodium citrate and 100 g. of anhydrous sodium carbonate in about 800 c.c. of water and then mixing the two solutions and making up to a litre.

**Barfoed's reagent.** 6.6 g. of cupric acetate and 1 c.c. of glacial acetic acid are dissolved in water and made up to 100 c.c.

**Borsche's reagent.** 1 % methyl alcoholic solution of 2 : 4-dinitrophenylhydrazine. Very valuable for detecting carbonyl groups.

1 g. of solid is refluxed with 100 c.c. of methyl alcohol till dissolved.

**Chromic acid mixture.** 10 g. of commercial chromic anhydride are dissolved in a mixture of 60 c.c. of water and 8 c.c. of concentrated sulphuric acid. 1 c.c. of the solution contains 0.05 g. of available oxygen. (A rough calculation of the reagent necessary for oxidising 1 g. of the substance should always be made before hand.)

**Denige's reagent** (Acid mercuric sulphate). 5 g. of mercuric oxide are dissolved in a solution of 20 c.c. of concentrated sulphuric acid and 100 c.c. of water while the mixture is still hot.

**Fehling's solution.** (1) 6.9 g. of copper sulphate crystals are dissolved in 40 c.c. of water and diluted to 100 c.c.

(2) 15 g. of sodium hydroxide and 36 g. of Rochelle salt are dissolved separately in 30 c.c. of water each, mixed and diluted to 100 c.c. after cooling.

Equal volumes of (1) and (2) are mixed before use.

**Hydroxylamine reagent for ketones.** (1) 7.25 g. of hydroxylamine hydrochloride are dissolved in 9 c.c. of water and diluted to 35 c.c. by adding absolute alcohol.

(2) 10 g. of pure sodium hydroxide are dissolved in 20 c.c. of water and diluted to 140 c.c. by adding absolute alcohol. One part of (1) and four parts of (2) are mixed before use.

**Iodine solution.** 2 g. of iodine, 10 g. of potassium iodide and 30 c.c. of water are ground together in a mortar till the solids have dissolved.

**Lucas's reagent for alcohols.** 13.6 g. of anhydrous zinc chloride are dissolved in 10.5 g. of concentrated hydrochloric acid.

**Mayer's reagent** (Potassium mercuri-iodide). 10 g. of potassium iodide and 2.8 g. of mercuric chloride are dissolved in 200 c.c. of water.

**Nylander's solution.** 4 g. of Rochelle salt and 2 g. of bismuth subnitrate are dissolved in 100 c.c. of 8% caustic soda.

**Potassium permanganate** for oxidation. 61.1 g. of permanganate are dissolved in a litre of distilled water. 1 c.c. of the solution contains 0.01 g. of available oxygen.

**Phenylhydrazine reagent.** (a) 4 c.c. of the pure light coloured base and 4 c.c. of glacial acetic acid are dissolved in 10 c.c. of water. Alternatively, 4 g. of phenylhydrazine hydrochloride are dissolved in 16 c.c. of water, 6 g. of sodium acetate crystals are added and one drop of glacial acetic acid. This composition is very useful for preparing the osazones of sugars.

(b) To test for ketones, 0.3 c.c. of glacial acetic acid, 7 c.c. of water, 2 c.c. of light coloured phenylhydrazine are mixed together. (This lasts for a few days only and should be made afresh.) 4 drops of the reagent are added to 1 drop of ketone in 2 c.c. of water or alcohol and the mixture heated by immersing in a boiling water-bath for 5 minutes.

**Sodium hypochlorite.** 100 g. of freshly made bleaching powder are ground into a thin cream with 450 c.c. of water and 84 g. of anhydrous sodium carbonate are added with stirring. The mixture is shaken well, and after keeping for some time, the precipitated calcium carbonate is filtered and the clear solution used.

**Saturated sodium bisulphite solution.** Sodium carbonate crystals (200 g.) are covered with water insufficient to dissolve them and sulphur dioxide is passed till the solid disappears and a pale green solution is obtained. On standing, this solution deposits crystals.

The solution prepared as described above is more effective than the commercial bisulphite and is recommended for use even in preparative work.

**Schiff's reagent.** 0.2 g. of pure fuchsin (p-rosaniline) as hydrochloride or acetate is dissolved in 20 c.c. of water and saturat-

ed with sulphur dioxide. After the solution has become colourless, it is filtered, diluted to 200 c.c. with water and preserved in dark bottles.

**Seliwanoff's reagent.** 0.05 g. of resorcinol is dissolved in 100 c.c. of concentrated hydrochloric acid and diluted with an equal volume of water.

**Tollen's reagent.** Commercial ammonia (sp. gr. 0.90) is diluted with an equal volume of water and 10 g. of silver nitrate are dissolved in 100 c.c. of this diluted ammonia. A 10 per cent aqueous solution of caustic soda is also prepared and kept separate. The two are mixed in equal volumes just before use.

### Organic chemicals

**Preparation of amylene.** In a 100 c.c. round-bottom flask 18 c.c. of water are taken and an equal volume of concentrated sulphuric acid added, the flask being cooled in running water during the addition. 18 c.c. of secondary amyl alcohol (2-pentanol) are now added and the flask fitted with a long condenser through which ice-water is circulating rapidly. An adapter is attached by means of a cork to the end of the condenser and the adapter allowed to dip into a flask surrounded by ice. The flask containing the alcohol-acid mixture is heated on a water-bath till no more liquid distils over. The distillate is treated with 10 c.c. of 5% caustic soda, shaken thoroughly and transferred to a separating funnel. The upper hydrocarbon layer is separated, dried over anhydrous calcium chloride and distilled. The portion boiling over at 35-41° is collected in a dry receiver. Yield, 6-7 g.

**Preparation of methylamine solution.** In a 250 c.c. flask fitted as for steam distillation, 9 g. of freshly made bleaching powder are placed and a thin paste of it is made by adding 25 c.c. of water. A cold solution of 2.5 g. of acetamide in 5 c.c. of water is next added and after thorough mixing a solution of 6 g. of sodium hydroxide in 25 c.c. of water is added. The mixture is steam distilled, and the methylamine coming over is absorbed in 10 c.c. of water till the distillate is no longer alkaline to litmus. This solution can be used for the reactions of aliphatic amines (p. 97).

**Preparation of 3 : 5-dinitrobenzoic acid.** 10 g. of benzoic acid are dissolved in 100 g. (53 c.c.) of concentrated sulphuric acid and fuming nitric acid (26 g.), i.e., 17.3 c.c. of sp. gr. 1.50,



are added in small portions with shaking. The mixture is heated on a boiling water-bath for about 8 hours and finally on a sand-bath till no more brown fumes are evolved. The nitrated mixture is poured into about a litre of ice-water. The crude 3 : 5-dinitrobenzoic acid that is precipitated is filtered, washed with water and purified by crystallisation from hot water or alcohol. M.P. 204°.

**Preparation of 2 : 4-dinitrophenylhydrazine.** 14 g. of hydrazine sulphate are suspended in 50 c.c. of hot water in a 250 c.c. beaker, stirred well and 35 g. of potassium acetate are added to precipitate the sulphate as potassium sulphate. The solution is boiled for five minutes, cooled slightly, and 30 c.c. of alcohol are added. The solid is filtered when cold and washed with 25 c.c. of hot alcohol. A solution of 20.2 g. of 2 : 4-dinitrochlorobenzene in 100 c.c. of alcohol is added to the hydrazine solution prepared as above contained in a 500 c.c. round-bottom flask and the mixture is refluxed with frequent shaking for about an hour. Most of the product crystallises out in about fifteen minutes after mixing. The substance is filtered, washed first with 25 c.c. of warm alcohol and finally with warm water to remove soluble salts. Evaporation of the filtrate furnishes an additional quantity of the product. Total yield, 17 g. 85% of theory.

### **Preparation of nitrosomethylurea.**

In a tared 1-l. flask is placed 200 g. (1.5 moles) of 24 per cent aqueous methylamine solution and concentrated hydrochloric acid is added until the solution is acid to methyl red ; about 155 c.c. of acid are required. Water is added to bring the total weight to 500 g., 300 g. (5 moles) of urea are added, and the solution is boiled gently under reflux for three hours and then vigorously for 15 minutes. The solution is cooled to room temperature, 110 g. (1.5 moles) of 95 per cent sodium nitrite is dissolved in it, and the whole is cooled to 0°.

The nitrosomethylurea rises to the surface as a crystalline foamy precipitate which is filtered at once with suction and pressed well on the filter. The crystals are stirred to a paste with about 50 c.c. of cold water, sucked as dry as possible and dried in a vacuum desiccator to constant weight. The yield is 105-115 g. (66-72 per cent of the theoretical amount.)

**Alternative method**

In a 1-l. flask 100 g. of methylamine hydrochloride, 80 g. of urea, 125 c.c. of water and a few drops of hydrochloric acid are placed and the solution is boiled for 3 hours under reflux on a wire gauze. The solution is cooled, 30 g. of sodium nitrite is dissolved in it and the whole is cooled to 0°. A mixture of 150 g. of crushed ice and 25 c.c. of concentrated sulphuric acid in a 2l. flask is surrounded by an efficient freezing mixture and the cold methylurea-nitrite solution is run in slowly with mechanical stirring at such a rate that the temperature does not rise above 6°.

The precipitate is filtered at once with suction and washed with cold water. The crystals are pressed well on the filter and sucked as dry as possible. The product is then stored in a refrigerator.

**Inorganic preparations****(a) Gases**

**Ammonia.** Ammonia is available in the form of liquefied gas stored in cylinders. If this facility is not available, small quantities of ammonia gas may be prepared by heating liquor ammonia. The liquor ammonia is placed in a round-bottomed flask fitted with an efficient reflux condenser. The gas issuing from the top of the condenser is dried by passing through a tower packed with soda lime and sent in to the reaction vessel after interposing a safety bottle.

**Chlorine.** Chlorine is commercially available stored in cylinders. Small quantities can be readily prepared by the action of concentrated hydrochloric acid on potassium permanganate. Finely powdered potassium permanganate is placed in a distilling flask whose neck is fitted with a separatory funnel. The side tube is connected to wash bottles containing water and concentrated sulphuric acid. 4.1 g. of chlorine are obtained from 3.7 g. of potassium permanganate and about 25 c.c. of concentrated hydrochloric acid are required for the reaction. When about half of the acid has been added, the evolution of gas slackens and the flask is warmed gently with shaking. When all the acid has been added, the mixture is boiled gently.

**Hydrogen chloride.** If large volumes of hydrogen chloride gas are required, it is desirable to make use of the following arrangement. 150 c.c. of concentrated sulphuric acid are placed in a 500 c.c.

separating funnel fitted with a two-holed cork. A separatory funnel of 150 c.c. capacity which has been fused to a capillary tube is fitted into one hole. The other hole is fitted with a delivery tube connected to a three-neck bottle containing concentrated sulphuric acid and fitted with a thistle funnel just dipping into the acid through the central neck. About 100 c.c. of hydrochloric acid are placed in the smaller separatory funnel. After filling the capillary portion with the hydrochloric acid, the capillary portion is allowed to dip well into the sulphuric acid layer. Hydrogen chloride is generated by running in the hydrochloric acid into the concentrated sulphuric acid. About 30 g. of hydrogen chloride may be obtained from 100 c.c. of the hydrochloric acid:

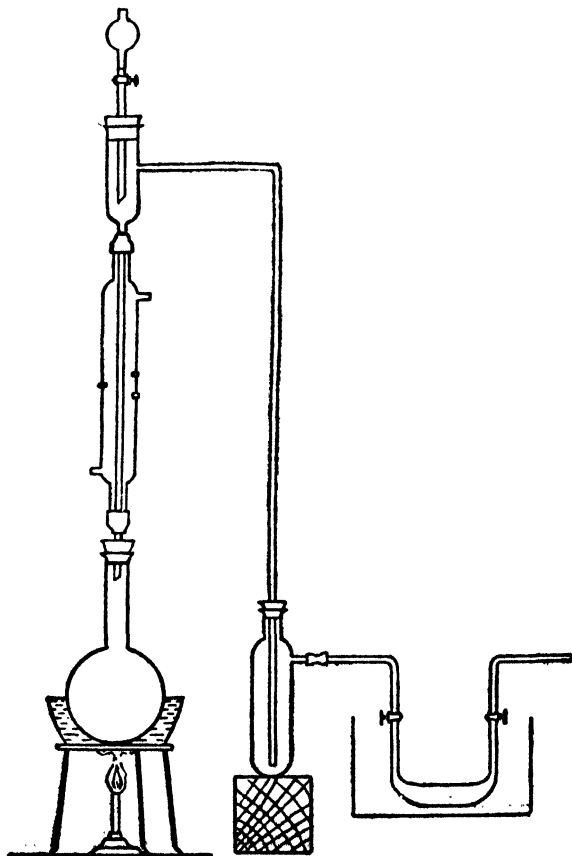


Fig. 86. Apparatus for preparation of carbonyl chloride.

**Hydrogen bromide.** Small amounts of the gas are best prepared by the action of bromine on dry tetralin. Bromine is allowed to drop into dry tetralin and hydrogen bromide is immediately evolved. Traces of bromine carried along with the gas are removed by bubbling it through a wash bottle containing dry tetralin.

**Phosgene.** The apparatus is assembled (Fig. 66) in a fume cupboard with a good draught because of the highly poisonous nature of phosgene. 100% sulphuric acid to which 2% by weight of ignited kieselguhr has been added is placed in the flask. The sulphuric acid is heated to 120-130° in an oil bath and the carbon tetrachloride is allowed to run in drop-wise from the separating funnel. The evolved phosgene passes through a wash bottle containing concentrated sulphuric acid and then into a receiver kept in a freezing mixture. After the completion of the reaction, the liquid phosgene in the receiver is warmed to 40° and the gaseous phosgene is led into a bottle containing toluene in which it is absorbed.

**Nitrogen.** Nitrogen is available commercially, stored in cylinders under pressure. Traces of oxygen present are removed by passing through Fieser's solution which is prepared as follows: To a solution of 20 g. of potassium hydroxide in 100 c.c. of water 2 g. of sodium anthraquinone sulphonate and 15 g. of commercial sodium hydrosulphite are added and stirred until dissolved. The blood red solution is ready for use when it has cooled down to room temperature.

#### (b) Liquids

**Thionyl chloride.** Commercial thionyl chloride often contains traces of acids and other impurities which interfere with the smooth conversion of an acid to an acid chloride unless they are removed by the following process. The thionyl chloride (50 c.c.) is mixed with 10 c.c. of quinoline and distilled using a short fractionating column. The distillate is then mixed with raw linseed oil and redistilled. The distillate is colourless and pure. The operations are best carried out in all-glass apparatus with exclusion of moisture.

**Hydrazine hydrate.** 40-50% solutions of hydrazine are available commercially. More concentrated solutions may be obtained by the following procedure. A mixture of 150 g. of the solution (40%) and 250 c.c. of xylene is distilled from a 500 c.c.

round-bottomed flask fitted with an efficient fractionating column. The corks are covered with tin foil. All the xylene passes over with about 85 c.c. of water. The residue is distilled, yielding about 50 g. of 90-95% hydrazine hydrate.

**Acid hydrobromic.** 25 c.c. of liquid bromine are suspended in about 150 c.c. of water contained in a 500 c.c. Erlenmeyer flask, cooled in ice and sulphur dioxide from a cylinder is passed in until a uniform pale yellow solution remains. On distilling this solution, water passes over at first and then the constant boiling mixture containing traces of sulphuric acid. This is redistilled with a little barium bromide and the fraction coming over at 126-127° is collected. The distillate has a density of 1.47 and contains 48% by weight of hydrogen bromide.

**Acid hydriodic.** This acid is invariably used for methoxyl estimation or for dealkylating aliphatic or aliphatic-aromatic ethers and also sometimes for reduction. The constant boiling mixture has a boiling point of 127°/760 m.m. containing 57% by weight of hydrogen iodide and a density of 1.70. If necessary, it can be prepared by saturating boiled water with the gas and diluting the solution with water to get the required density. It is available commercially in sealed tubes but often contaminated with free iodine. For a quantitative estimation, the acid is purified by careful distillation over a little red phosphorus.

### (c) Solids

**Aluminium-mercury couple.** This should be prepared just before use. Pure aluminium foil, cut into thin strips, or even aluminium turnings are freed from oily matter by first washing with alcohol and then with ether and dried in the air oven. They are placed in a saturated solution of mercuric chloride for a minute or two, when the aluminium gets coated with a film of mercury; the liquid is poured off, the couple washed with cold water, then with alcohol and finally with benzene.

**Anhydrous aluminium chloride.** (Conduct the preparation in the hood.) When required for organic syntheses this reagent should be prepared fresh. It is most conveniently obtained in large quantities by using the combustion furnace used for carbon and hydrogen determination. The combustion tube, 80 cm. long, having a diameter of 19 m.m. (externally) is drawn out to a taper at one of its ends and a loose plug of freshly ignited

asbestos is pushed from the wider open end to very near the drawn out portion. Aluminium turnings cleaned as in the previous preparation are introduced till the tube is about three-quarters full and another loose plug of asbestos is pushed in so that it is at a distant of about 5-6 cm. from the open end. The tube is placed horizontally on the table and tapped gently till there is a clear passage over the turnings throughout the entire length of the tube between the asbestos plugs. The tube is placed on the combustion furnace (Pt. II) so that it projects at least 5 cm. beyond the furnace at either end. The drawn out part is connected to the source of pure dry hydrogen chloride. The aluminium chloride is received in a wider tube 50 mm. diameter fixed by a cork to the combustion tube and closed at the other end by a one-holed cork carrying a calcium chloride tube. The cork should be protected from the heat of the furnace by an asbestos sheet, perforated and slipped on the combustion tube before passing this through the cork. Having fitted up the apparatus, the air in the tube is first displaced by sending in a rapid stream of dry hydrogen chloride for about ten minutes, and the burners are lighted all of them with a low flame to begin with. Commencing from the inlet end the tube is raised to a low red heat gradually, turning the burners on to a full flame in threes and fours till the metal burns away completely and the aluminium chloride sublimes into the receiver. It is necessary to heat the projecting portion of the tube and the receiver now and then by a burner to prevent clogging of the tube. If at any stage of the heating, the stream of hydrogen chloride ceases to bubble through the wash bottles, the tube must be clogged somewhere and this needs examination before proceeding further. As soon as the experiment is over the still warm aluminium chloride is scraped out into a wide-mouthed bottle which is tightly stoppered and kept in a desiccator over concentrated sulphuric acid.

Dry hydrogen chloride is conveniently obtained thus : In a filter flask of 750 c.c. capacity, a layer of common salt about 3 ins. is placed and crude concentrated hydrochloric acid is poured in so that the flask is nearly one-third full. The flask is fitted with a one-holed rubber stopper carrying a dropping funnel of 250 c.c. capacity containing concentrated sulphuric acid. The sulphuric acid is dropped slowly and the stream of HCl gas which escapes through the side-tube is dried by passing through two wash bottles containing concentrated sulphuric acid.

Theoretically, 25 g. of aluminium should give 123 g. of the anhydrous chloride but usually no more than 80-90 g. can be obtained.

**Bleaching powder.** 100 g. of freshly burnt quicklime are slaked with the minimum amount of water and the slaked lime obtained as powder is introduced into a 500 c.c. round-bottom flask, the neck of which is loosely plugged with cotton. The flask is immersed in cold water and chlorine is led into the flask which is turned over every now and then in order to expose a fresh surface to the action of the chlorine. It takes nearly three to four hours for an efficient preparation. The product may be preserved in a stoppered bottle but slowly deteriorates.

The evaluation of the sample for available chlorine is done as follows : 2-3 g. of the sample are accurately weighed into a mortar, ground up finely with water and transferred to a 250 c.c. measuring flask. The contents of the mortar are washed into the flask and finally diluted to the mark with water. 25 c.c. of this turbid solution are pipetted out into a beaker, 20 c.c. of a solution containing 2 g. of potassium iodide and an excess of acetic acid are added and the liberated iodine titrated at once with standard thiosulphate. 1 c.c. of N/10 thiosulphate = 0.003546 g. of chlorine.

**Copper powder.** 50 g. of copper sulphate crystals are dissolved in 150 c.c. of water in a beaker and while the cooled solution is stirred mechanically, good zinc dust or spangles (16 g.) are very gradually added (1 hour) till the solution is decolourised. The precipitated copper is washed by decantation with water. The excess of zinc is destroyed by agitation with dilute hydrochloric or sulphuric acid till there is no further evolution of hydrogen. The powder is filtered and preserved in a moist condition in a stoppered bottle.

**Cuprous chloride.** 31 g. of cupric chloride crystals are dissolved in the minimum amount of water and sulphur dioxide is passed till reduction is complete as shown by the loss of colour. The precipitate is filtered, washed first with sulphurous acid and then with glacial acetic acid till the filtrate is colourless. The cuprous chloride is transferred to a porcelain basin and heated on a water-bath till the acetic acid is driven off. It is preserved in a tightly stoppered bottle.

For the Sandmeyer reaction, the precipitate may be dissolved

immediately in a mixture of 100 c.c. of concentrated hydrochloric acid and 50 c.c. of water.

**Chromic anhydride.** To 1 volume of a cold saturated solution of potassium chromate or sodium dichromate, 1.5 volumes of concentrated sulphuric acid are added gradually with constant stirring. On cooling the mixture in ice, crystals of the anhydride separate. The liquid is decanted, the crystals are washed by decantation with a little nitric acid and dried on a porous plate in a desiccator. The anhydride crystallises in scarlet needles and is very hygroscopic.

**Lead peroxide.** 20 g. of lead acetate are dissolved in 100 c.c. of water and 100 c.c. of 4N sodium hydroxide are added to the above solution. Chlorine gas is then passed till a drop of the solution withdrawn and acidified with hydrochloric acid does not give a precipitate with hydrogen sulphide. The mixture finally assumes a dark brown colour and the precipitate of lead peroxide is filtered off, washed with water, then with dilute nitric acid and finally with water till free from acid.

Instead of passing chlorine, the lead acetate solution may be heated and then treated with a filtered solution of bleaching powder (40 g. in 600 c.c. of water) gradually till the precipitate turns dark brown and no further precipitation occurs on adding more bleaching powder solution. The liquid is decanted and the precipitate washed by decantation several times with water, filtered, washed again with water and preserved as a thick paste in a well-stoppered bottle.

*Estimation.* 0.2 to 0.5 g. of the paste is accurately weighed into a glass-stoppered bottle containing 100 c.c. of concentrated hydrochloric acid, 20 to 25 g. of sodium chloride and 1 g. of potassium iodide. The mixture is well shaken for a few minutes to ensure complete decomposition and the liberated iodine is titrated at once with N/20 thiosulphate. 1 c.c. of N/20 thiosulphate = 0.006 g. of pure lead peroxide.

**Platinum oxide.** A solution of 3.5 g. of pure chloroplatinic acid in 5 c.c. water taken in a 450 c.c. beaker is treated with 35 g. of A.R. sodium nitrate. The mixture is evaporated to dryness by gently heating with a Bunsen flame while stirring with a glass rod. The temperature is then raised to 350-370° within about 10 minutes. The mass fuses with evolution of brown fumes and



separation of a precipitate of brown platinum oxide. If foaming occurs, the mass is stirred more vigorously and an additional burner is directed at the top of the reaction mixture. After 15 minutes, when the temperature has reached about  $400^{\circ}$ , the evolution of gas decreases considerably. The heating is continued with the full force of the Bunsen burner, so that the temperature is about  $500-550^{\circ}$ . The mass is maintained at this temperature for about 30 minutes. The mass is then allowed to cool, and treated with 50 c.c. of water. The brown precipitate of platinum oxide is washed once or twice with water by decantation, filtered on a sintered funnel and washed on the funnel with water until practically free from nitrates. The washing is stopped as soon as there is a tendency for the precipitate to become colloidal. The platinum oxide is dried in a vacuum desiccator.

**Palladium on carbon.** The activated carbon (commercial varieties like Norit or Darco) is first heated on a steam-bath with 10% nitric acid for 2-3 hours, washed free from acid and dried at  $100-110^{\circ}$ . A suspension of 41.5 g. of this acid-washed carbon in 600 c.c. of water in a 2-litre beaker is heated to  $80^{\circ}$ . A solution of 4.1 g. of palladium chloride in 10 c.c. of concentrated hydrochloric acid and 25 c.c. of water is prepared by heating on a water-bath for 2 hours until solution is complete. This solution is added to the suspension of the carbon followed by 4 c.c. of 37% formaldehyde solution. The mixture is stirred mechanically and rendered alkaline to litmus by the addition of 30% sodium hydroxide solution, the stirring being continued for a further five minutes. The catalyst is filtered off on a Buchner funnel, washed ten times with 125 c.c. portions of water and dried in a vacuum desiccator at room temperature over calcium chloride. The catalyst is stored in a tightly stoppered bottle.

### **Raney Nickel Catalyst**

38 g. of sodium hydroxide dissolved in 150 c.c. of distilled water taken in one litre beaker and cooled to  $10^{\circ}\text{C.}$  in an ice bath.

30 g. of Ni-Al alloy are added in small portions with vigorous stirring so that the temperature does not rise above  $25^{\circ}\text{C.}$  After all the alloy has been added the beaker is taken out and kept at room temperature, till the evolution of hydrogen becomes slow. It is then heated on a steam bath for 8 to 12 hours.

The solution is decanted and treated with 5 g. of sodium

hydroxide in 50 c.c. water. After the liquid is decanted and the nickel is washed by suspension in distilled water 20 to 40 times till washings are neutral to litmus.

The catalyst is finally washed 3 times with 20 c.c. of 95% alcohol and stored under absolute alcohol.

**Silver powder** (from silver residues). The silver residues are treated with a slight excess of dilute hydrochloric acid to convert them all into silver chloride which is filtered off and well washed with hot water. The washed silver chloride is transferred to a big porcelain basin (10 ins. diam.), suspended in warm dilute sulphuric acid and pieces of pure zinc foil are added. The zinc gradually goes into solution and the silver chloride gets reduced to silver. The excess of zinc is dissolved by adding dilute sulphuric acid and the silver powder is filtered, washed with dilute sulphuric acid and finally with distilled water. The silver is dissolved in dilute nitric acid and reprecipitated as chloride by adding a slight excess of dilute hydrochloric acid. The silver chloride precipitate is washed with water by decantation and while still moist is added to a solution of sodium hydroxide (15%) kept boiling in a porcelain dish. A few c.c. of a concentrated solution of glucose are added to the above liquid from time to time until a sample of the grey silver powder dissolves clear in nitric acid. The precipitate is filtered, washed with cold water, then with concentrated ammonia and finally with water. The silver powder is dried on the water-bath.

**Stannous chloride** (Anhydrous). 123 g. of pure stannous chloride dihydrate are added to 102 g. of freshly distilled acetic anhydride with good stirring. Much heat is evolved and the reaction is best conducted in a fume cupboard. After one hour, the anhydrous stannous chloride is filtered off, washed free from acetic acid with two 30 c.c. portions of anhydrous ether, and dried overnight in a vacuum desiccator.

**Sodium wire.** For some experiments sodium is used in the form of wire obtained by employing a press (Fig. 67).

The sodium is scraped by means of a clean knife to free it from the outer crust of oxide and cut into large pieces of a size capable of being slid easily into the hollow of the press. The pieces are pressed between folds of paper to remove the adhering

kerosene and the handle worked by a screw is turned so that the

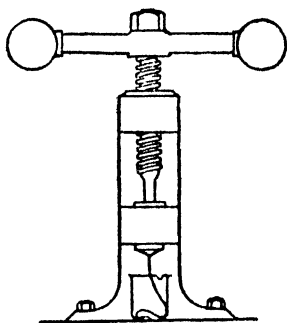


Fig. 67. Sodium press.

sodium comes out as a continuous wire by being forced through a small opening. The wire is received in a porcelain dish or a wide-mouthed bottle containing some dry petroleum ether instead of kerosene. After use the residual sodium sticking to the press is carefully removed by means of a knife and any bits sticking tenaciously are destroyed by wiping with a cloth soaked in methyl alcohol. The press is then thoroughly cleaned, dried and

smeared with a light coating of vaseline.

**Sodium acetate (anhydrous).** The commercial product contains water. It is melted in a porcelain basin over a low flame ; water is lost and it gradually solidifies. The heating is continued with a larger flame till the mass melts again. At this stage carbonisation may occur and should be avoided by taking care not to heat too strongly. The liquid is poured into a clean dry mortar and powdered after it solidifies. It is preserved in a stoppered bottle, preferably in a desiccator.

**Sodium amalgam.** 200 g. of mercury are warmed in a porcelain basin on a water-bath for fifteen minutes and transferred to a dry mortar. Five grams of sodium are well scraped and cut into small pieces, say 3 mm. square. Each piece is dried between filter paper and introduced by the pointed end of a file under mercury and kept pressed with the pestle. The sodium pieces dissolve with a bright flash. The amalgam is broken up and transferred into a dry, stoppered wide-mouthed bottle.

If an iron mortar is available the preparation of sodium amalgam may be carried out conveniently by the following procedure. The iron mortar is provided with a lid of asbestos sheet. The mercury is placed in the mortar, the sodium added in one lot and the mortar covered with the asbestos sheet. There is an instantaneous reaction, the amalgam being liquid due to the heat evolved. The amalgam is powdered as it solidifies by using an iron pestle. The preparation is best carried out in the open air.

**Selenium dioxide.** Commercial selenium dioxide is best purified by sublimation. The crude selenium dioxide is placed in a large porcelain crucible covered with two nested funnels. The crucible is heated with a small flame until the sublimation is complete. When the crucible has cooled, the sublimate is removed and stored in a tightly stoppered bottle. The operation should be carried out in a fume cupboard and extreme care should be taken because of the poisonous properties of selenium dioxide.

**Zinc cyanide.** A solution of 150 g. of anhydrous zinc chloride in the minimum volume of 50% alcohol is treated rapidly and with good stirring with a solution of 100 g. of sodium cyanide (97-98%) in 125 c.c. of water. The precipitated zinc cyanide is filtered, drained well, washed with alcohol and then with ether. It is dried in a vacuum desiccator and preserved in a tightly stoppered bottle.

**Evaluation of zinc dust.** When it is known definitely that iron is absent in the sample or is present only in traces, 0.25 to 0.5 g. is accurately weighed into a 250 c.c. stoppered bottle and shaken with 50 to 60 c.c. of a nearly saturated solution of pure ferric alum. 25 c.c. of concentrated sulphuric acid is added gradually with continuous cooling and the solution transferred to a measuring flask (250 c.c.). The bottle is washed with small quantities of dilute sulphuric acid and the washings added to the flask. The solution is finally made up to the mark and an aliquot part titrated against N/10 permanganate. 1 c.c. of N/10  $\text{KMnO}_4 \equiv 0.00327$  g. zinc.

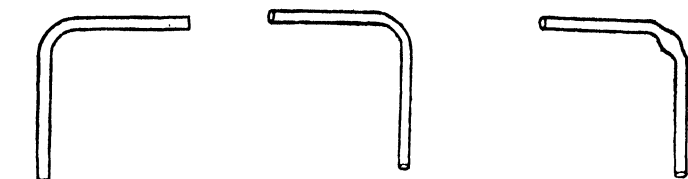
## CHAPTER XIII

### GENERAL MANIPULATION

**Boring of corks.** Wooden corks are to be preferred to rubber ones since most organic liquids attack rubber. A good cork free from holes is chosen, moistened with a little water and the cork is softened by means of a cork-press or by rolling it under the foot. A sharp cork borer with the diameter a trifle smaller than that of the tube to be pushed in, is selected and while the cork is held in the left hand the borer is turned gently with the right until it is about half way through. The cork should also be turned during each twist of the borer. The borer is removed by a screw motion, the piece of cork inside the borer is pushed out and the boring commenced from the other end at exactly the opposite spot. In this way a clean bore can be made. By improper holding of the cork the boring generally comes out slantwise and the tube when inserted into the cork presents an awkward appearance. Any enlargement of the bore if required is effected by running a round file through the hole while the cork is turned continuously. The tubes should be introduced with moderate pressure after slightly moistening with water or a light smear of glycerine. Pushing forcibly a tube of a larger diameter into a hole of smaller bore is always to be avoided as during the process the tube is liable to break and cause injury to the hand. The same precaution is to be observed in inserting a thermometer into a bored cork. Any alteration in the position of thermometer or glass tube, when once the apparatus has been assembled, should be done only after disconnecting and not with the apparatus intact.

**Glass work : Bending of glass tubes.** This is very important if the apparatus set up is to have an elegant appearance. The tube is held lengthwise in a batwing or fishtail flame and kept turning till it is soft. The tube is removed from the flame and bent to the desired angle by applying gentle pressure. The bend should be round and strong and never angular. The edges of the tube should be fire polished by holding them in the non-luminous flame of a Bunsen burner till they just melt.

Pyrex glass which has a higher softening temperature can be bent only in the blast lamp.



Correctly bent tube.

Badly bent tube.

Fig. 68.

### Exercise

Set up a steam distillation apparatus paying particular attention to the bending of glass tubes and the boring of corks. (See Fig. 17.)

**Drawing of melting point tubes.** Soft soda glass tubing, 1 cm. diameter, or broken test-tubes can be used for this purpose. The latter are cleaned with chromic acid, washed with water and dried. The tubing is heated in a blast lamp while gently rotating until it becomes soft enough for drawing. The tube is removed from the flame, momentarily cooled and carefully drawn out to a long capillary about 2 feet in length. The wider portion can be similarly treated until a capillary tubing of about 2 metres length is obtained. Portions of the tube, 6-7 cm. long and 1-2 mm. bore, are cut off and preserved in a stoppered tube to be used when necessary.

**Cutting glass tubes.** Smaller sizes of tubing up to 10 mm. can be cut by making a clean mark with a sharp file at the point to be separated; holding the tube with both hands near the file mark the tube is pulled apart. A clean separation can thus be obtained. Larger sizes can be cut by making a file mark as before and pressing the pointed end of a drawnout glass rod heated to redness on the file mark. If the glass tube does not break after treating once or twice like this, a drop of water will produce a crack which should be carried round by the judicious use of the hot rod.

**Cutting hard glass tubes.** To cut hard glass tubing a deep file mark is made and on each side of the mark two strips of moist filter or blotting paper within about 0.5 cm. of each other are

wrapped round the tube. The space between the rolls of paper is then heated by a small pointed blow pipe flame which is directed so as to strike only the top of the tube while the latter is turned on. If the tube does not crack across, it is strongly heated and a drop or two of water are allowed to fall on the mark. This generally produces a clean cut.

Glass blowing to the extent of making T-pieces, test-tubes with side-tube or small distilling flasks of capacity about 10-15 c.c., is a very necessary acquisition to the student of practical organic chemistry. Success in this direction is a matter of skill acquired by constant practice in the rudiments of glass blowing such as :

- (1) closing one of the ends of an open glass tube.
- (2) joining two pieces of glass tubing of equal and unequal diameters.
- (3) blowing small bulbs at the end of a tube.

### Exercise 1

#### To make a T-piece

(1) Draw out a 10 in. length of tube of 5 mm. bore at a distance of about 4 in. from one end. Snap the tube into two at the capillary part and seal up the capillary ends.

(2) When the tubes have cooled, heat at the middle of the longer piece at one spot with a pointed flame till it shows signs of collapse. Remove the tube from the flame and expand the softened part by gently blowing.

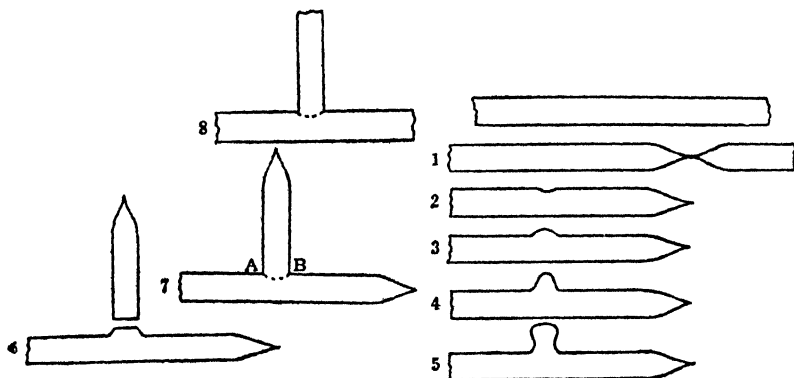


Fig. 69. Stages in making a T-piece.

(3) Alternately heat and blow gently till a cylindrical attachment is built up, the tube still remaining closed.

(4) By sharp heating and blowing, open out at the cylindrical attachment.

(5) Heat the opened part and the wider end of the other piece simultaneously with rotation and when both are evenly and equally red hot, press the two portions together carefully, and blow from the open end of the longer piece gently. Work up the joint by alternately heating and blowing till the joint is uniform.

## Exercise 2

### To make a test-tube with side-tube

(1) Cut out 1 foot length of glass tube of 14-16 mm. bore from a longer tube. At a distance of 2 in. from each end draw out the tube to a capillary.

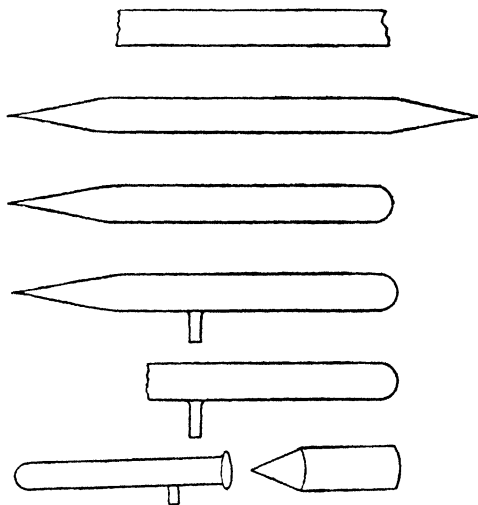


Fig. 70. Stages in making a test-tube with side-tube.

(2) Close one end as usual so that it is quite hemispherical.

(3) At a distance of about 5 in. from the closed end join a short glass tube of three to four inches and of bore 5-6 mm, so as to make a T-piece as in Ex. 1.

(4) Cut off the wider tube with the side-tube fused to it so that its length is 6 in. Rotate the open end in the flame till



the glass has become soft and is somewhat dull red hot. Holding a charcoal cone on the left, turn the hot edge of the tube over the cone twice so that a rim is formed. The side-tube can then be cut off to have a length of 2 in. and fire-polished.

### Exercise 3

#### To make a small distilling flask

(1) Cut off a length of 10 in. of glass tube of 12-14 mm. bore and close one end of it as usual. Hold the tube horizontally in a larger flame and heat 1 cm. length of it at the sealed end till the glass melts completely and is red-hot. Remove the tube from the flame and blow gently keeping the tube horizontal and rotated all the while so that a bulb of about  $\frac{1}{2}$  to  $\frac{3}{4}$  in. diameter is formed.

(2) Blow a second bulb on the top of the first using another cm. length of the tube. This procedure is to accumulate glass so that the final bulb blown may not be too thin.

(3) Heat the bulbs over a larger flame with continuous and gentle rotation so that they coalesce into one. Remove from the flame and blow strongly at first and gently as the bulb swells, till

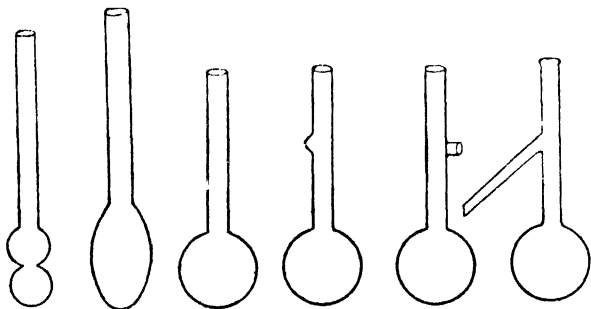


Fig. 71. Stages in making a small distilling flask.

the diameter of the bulb is about 1.5 inches. Cool the bulb and to see if it is strong, drop it on the table from a height of about one foot, when it should not break.

(4) Open out the bulb tube at a distance of about 3 in. from the bulb and attach a 6 inches length of tube of bore 5 mm. as described in Ex. 1. The cylindrical junction in this case is worked up so as to have an acute angle instead of a right angle.

(5) After attaching the side-tube, the wider tube with the bulb is cut off so that the neck of the distilling flask is about 5 in. Widen the open end of the neck as in the previous exercise.

**Exercise. 4****Sealing a Carius tube**

Carius tubes for halogen determination are closed at one end and generally are thick walled so as to withstand a high internal pressure. After the materials have been introduced into the tube the open end of the tube has to be sealed before placing it in the furnace.

(1) Heat the open end of the tube holding it with the left hand for about 5 minutes with constant motion in the smoky flame of the blowpipe. Then turn on the air blast slowly and heat strongly with gentle rotation till the tube becomes soft. Attach a piece of glass rod 4 in. long, heated in the flame till it has become soft, to the open end of the Carius tube by pressing and heating in the flame once again till a good joint is obtained.

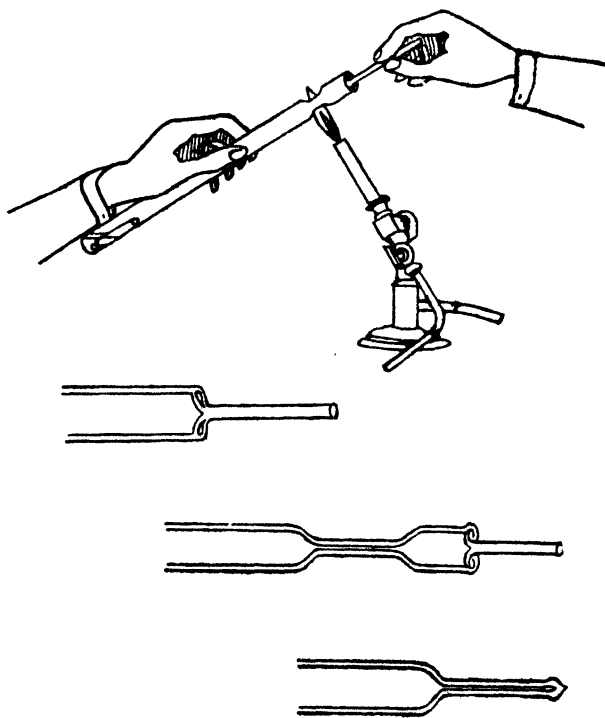


Fig. 72. Sealing a Carius tube.

(2) Heat the tube 2 in. from the open end with constant rotation to a length of about 1 in. over a large flame. Rotate the

tube with the glass rod serving as a support, without drawing the tube till the walls of the tube collapse uniformly and a thickening is produced. When the diameter is reduced to about 3 or 4 mm. draw out slowly so that a strong walled capillary about 2 in. long, is formed. The capillary part is then thickened by revolving in the flame and sealed off so that the seal is not thin.

This procedure may be adopted for sealing tubes when carrying out reactions under pressure.

**Preservation of liquid specimens in sealed tubes.**

Liquid specimens can be preserved best in sealed test-tubes (6 in.  $5/8$  in.), or boiling tubes (6 in.  $\times$  1 in.) A glass rod is attached to the mouth of the tube as described in Ex. 4 and the tube drawn out at a distance of about 1 in. from the mouth so that a strong walled capillary of length about 2 to 3 cm. is formed. The liquid to be introduced is poured through a drawn out funnel made from a test-tube. Any adhering liquid is removed by means of filter paper and the constricted part sealed by heating in the flame till the walls collapse of their own accord and a little glass has accumulated near the seal. At this stage the mouth of the tube sticking to the seal is drawn off.

A student should have ample opportunities of practising the art in the laboratory by utilising broken glass apparatus as much as possible instead of throwing them away.

**Opening sealed tubes or bottles.** Substances such as anhydrous aluminium chloride, sodamide and somewhat rarely phosphorus pentachloride which are preserved usually in sealed tubes, are found to develop high pressure due probably to atmospheric moisture. Great care should be exercised in opening such tubes as severe explosions may take place. The tubes are wrapped in thick cloth so that about an inch of the sealed part projects out. A neat file mark is made about midway in the exposed part and the mark touched with a red hot pointed glass rod. The piece detaches itself usually with a sharp report and even if the tube should break to pieces, the substance can be quickly separated from the glass pieces and transferred to a dry bottle kept ready for the purpose. The eyes may be protected by goggles.

**Preservation of highly volatile liquids.** Volatile liquids frequently used in the laboratory, such as methyl iodide, are best preserved in ground capped ether bottles.

**Cooling baths.** Finely crushed ice is used for maintaining reaction temperatures between  $0-5^{\circ}$ . A mixture of one part of common salt with three parts of ice will produce a temperature of about  $-20^{\circ}$ , but in practice the ice-salt mixtures give temperatures in the range of  $-5^{\circ} - 18^{\circ}$ . Temperatures of  $-40^{\circ}$  to  $-50^{\circ}$  may be reached with 5 parts of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and 4 parts of crushed ice.

**Gas absorption traps.** In certain reactions large volumes of acid fumes are evolved and it is desirable to minimise the nuisance by dissolving out the evolved gases by using suitable absorption traps, of which one type is illustrated in figure below :

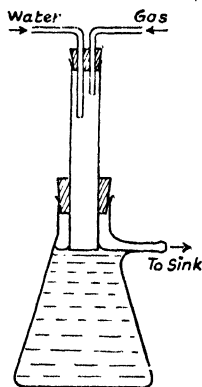


Fig. 73.

**Mechanical agitation.** Many organic preparations require mechanical stirring and several commercial electrically operated stirrers are available, which are rather costly. Considerable saving can be effected by purchasing a  $1/30$  H.P. motor and having it suitably mounted in conjunction with a rheostat for variation of speed.

The stirrers themselves are made from glass rod in any shape desired. One particular type, known as the Hershberg stirrer is useful for efficient agitation in round-bottomed vessels, even of pasty mixtures. It consists of a glass rod to which a glass ring is sealed. The glass ring is threaded with nickel or nichrome wire of about 1-2 mm. diameter as shown in

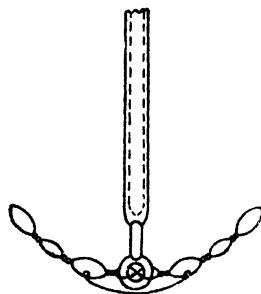


Fig. 74

the figure. The stirrer is easily introduced even through a narrow neck and in motion follows the contour of the flask.

**Mercury-sealed stirrers.** In certain organic preparations, mechanical stirring has to be effected with exclusion of moisture from the system. It is necessary in such cases to employ a mercury-sealed stirrer. Two types of mercury-sealed stirrers are illustrated in the figures below.

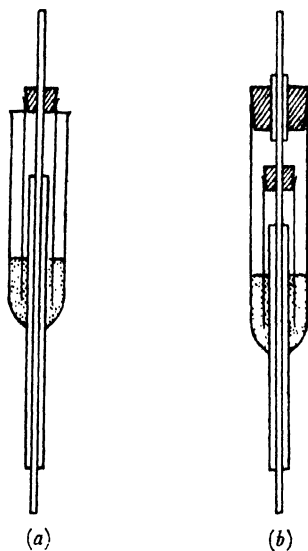


Fig. 75

ALCOHOLS: Their boiling points and the melting points of their derivatives.

Name of Alcohol	B.P.	Derivatives			Phenyl urethane	$\alpha$ -Naphthyl urethane
		3 : 5-Dinitro Benzoates	p-Nitro-Benzoate			
Methyl alcohol	66°	107°	96°		47°	124°
Ethyl "	78	92	57		52	79
Iso-propyl "	83	122	110		90	78
Tert-Butyl "	83	142			136	101
n-Propyl "	97	73	35		58	80
Tert-Amyl "	102	117			42	71
Iso-butyl "	108	87	67		80	104
n-Butyl "	117	64	35		57	71
Iso-amyl "	130	62			55	67
n-Amyl "	138	46	54		46	76
n-Hexyl "	160	58			42	59
Cyclohexanol	160	112			82	128
Ethylene glycol	197			Dibenzoate 73	157	176
Benzyl alcohol	205	112	84		78	134
Glycerol	294		192	Tribenzoate 76	180	191

PHENOLS : Their melting or boiling points and the melting points of their derivatives.

Name of Phenol	M.P.	B.P.	Acetates		Benzoate	Aryl Oxy-acetic acid	Bromo-Derivative		Picrates	Colour with ferric chloride
			M.P.	B.P.			M.P.	M.P.		
o-Chlorophenol	...	175°				145°	Tribromo	95°	83°	Violet.
Phenol	42°	180	195°		69°	99	Dibromo	56	88	Blue changing to yellow.
o-Cresol	...	190	208			151				
o-Bromophenol	...	195				143	Tribromo	95		Blue changing to blue violet : becomes turbid.
p-Cresol	36	202	208		71	136	Dibromo	49		
m-Cresol	...	202	212		54	102	Tribromo	84	88	Blue-violet.
p-Chlorophenol	...	217	228		86	155				
Eugenol	...	254	31		69		Tetrabromo	118		Yellowish green but blue in alcoholic solution.
o-Nitrophenol	44		39		142		4 : 6 Dibromo	117		Green (in alcoholic solution.)
Thymol	50	232	244		32	149	Bromo	55		

p-Bromophenol	...	63	236	21	102	157	Tribromo	95	189	
α-Naphthol	...	94	280	46	56	191	2 : 4 Dibromo	105		
m-Nitrophenol	...	97			95		Dibromo	91		
Catechol	...	104	245	64 (di-)	84 (di-)		Tetrabromo	192		Emerald green changing to red or violet, on adding NaHCO <sub>3</sub> .
Orcinol	...	108	287	25 (di-)	88 (di-)		Tribromo	104		Violet blue.
p-Nitrophenol	...	114		82	142		2 : 6 Dibromo	142		
Resorcinol	...	118			117 (di-)	273 (di-)	4 : 6 Dibromo	112		Dark violet.
β-Naphthol	...	122		70	106	153	Bromo	84	156	Faint green with white precipitate.
Pyrogallol	...	133	293	165 (tri-)	89 (tri-)		Dibromo	158		Orange red.
Hydroquinone	...	170		123 (di-)	199 (di-)		"	186		
Phloroglucinol	...	218		105 (tri-)	173 (tri-)		Tribromo	151		Brown changing to violet or red with NaHCO <sub>3</sub> .



## ALDEHYDES

Aldehyde	M.P.	B.P.	Oxime M.P.	Semi- carbazone M.P.	Phenyl hydrazone M.P.	2 : 4-Dinitrophenyl-hydrazone		
						Solvent for Preparation	Colour	M.P.
Formaldehyde	...	21°	47°	169°		Alcohol	Yellow	166°
Acetaldehyde	...	21		162	270°	"	Orange-yellow	168
Propionaldehyde	...	50		89		"	Orange	154
Acrolein	...	52					Orange-red	165
Isobutyraldehyde	...	64		125			Yellow	182
n-Butyraldehyde	...	74	56	126			"	122
Chloral	...	98						
Paraldehyde	...	124		222				
Benzaldehyde	...	179	35	232	158	Acetic acid	Orange	237
Salicylaldehyde	...	196	57	232	142	"	Light red	252 d
Cinnamic	...	220 d	138	215	168	"	Red	255 d
Hydrocinnamic	...	224	94	127				
Anisaldehyde	...	247	92	203	120	"	Orange-red	253-254 d
Piperonal	...	263	110	230	100	"	Red	266 d
o-Nitrobenzaldehyde	...	37°	103	256	156	Xylene	Yellow	250 d
m-Nitrobenzaldehyde	...	58	120	246	120	Acetic acid	"	292-293 d
Vanillin	...	80	117	229	105	"	Red	271 d
p-Hydroxy benzaldehyde	...	115		224	177	"	Purple-red	280 d
p-Nitrobenzaldehyde	...	106	129	221	159		Orange	320

## KETONES

Ketones	M.P.	B.P.	Oxime M.P.	Semi- carbazone M.P.	Phenyl hydrazone M.P.	2 : 4-Dinitrophenyl-hydrazone		
						Solvent for Preparation	Colour	M.P.
Acetone Diacetyl	...	56° 88	59° 75 (mono-) 245 (di-) 69	187° 278	42° 245	Alcohol Anisole	Yellow Orange	126° Above 300 charrs.
Diethyl Ketone	...	102	139	139		Alcohol	Pale Orange	156
Methyl ethyl ketone	...	80	135	135		"	Orange	110-111
Cyclohexanone	...	155	90	166	77	Acetic acid	Yellow	162
Acetophenone	20°	200	59	198	105		Orange-red	249-250*
Methyl p-tolyl ketone	...	222	85	205	94			
Benzophenone	...	305	141	164	137	"	Orange	238-239
Benzal acetone	...	41	115	187	157	"	Red	227
Benzal acetophenone	...	62		168		"	Orange-red	244 d
Thymoquinone Benzil	...	232	162 137	202 182	93 225	Alcohol	Yellow	180 189
	95		(mono-) 237 (di-) 153	(mono-) 244 (di-) 206 d	(di-) 106			
Benzoin	130					"	"	245

\* 238°-240° from alcohol.

## ACIDS

Acid	M.P.	B.P.	Ethyl ester		Methyl ester		Anilide M.P.	p-Tolu- ide M.P.	Amide M.P.
			M.P.	B.P.	M.P.	B.P.			
Formic Acid	...	101°		55°		32.5°	47°	53°	
Acetic Acid	16°	118		78		57.5	115	147	82°
Propionic Acid	...	140		99		79	103	124	79
Acrylic	...	140		101		85	104	141	84
Isobutyric	...	155		110		92	105	104	129
n-Butyric	...	163		120		102	90	72	114
Lactic	...			154		145	59		74 102(mono-) 156(di-)
Malic (d)	100				79°				210
Citric (hydrated)	101		294						419 d
Oxalic	101		186		51		245	267	140
o-Toluic	102		220			213	125		130
Benzoic	121		212			199	160	158	
Cinnamic	133		271		36		153		141

## BENZENOID HYDROCARBONS

Hydrocarbons	M.P.	B.P.	Nitration product		Sulphonyl derivatives		Picrate
			Position	M.P.	Chloride M.P.	Amide M.P.	
Benzene	5°	80°	1 : 3 Dinitro	90°	14°	148°	84°
Toluene	...	110	2 : 4 Dinitro	70	69	137	88
Ethyl benzene	...	135	2 : 4 : 6 Trinitro	37			96
p-Xylene	13	138	2 : 3 : 6 Trinitro	137	25	147	90
m-Xylene	...	139	2 : 4 Dinitro	83	para- 4, Sulpho- compound	137	91
o-Xylene	...	142	4 : 5 Dinitro	71	51	144	88
Cumene	...	153	2 : 4 : 6 Trinitro	109	"	107	
Mesitylene	...	163	2 : 4 Dinitro	86	57	141	97
Pseudocumene	...	168	2 : 4 : 6 Trinitro	231			
p-Cymene	...	175	3 : 5 : 6 Trinitro	185	61	181	97
Naphthalene	80	218	2 : 6 Dinitro Trinitro	54 118			
Phenanthrene	100	340	1 (α, nitro)	59			149 Colour yellow. Solvent alcohol
Anthracene	217						145 Colour " 138 Colour red. Solvent benzene.

p-nitrotoluene M. P. 54.

## AQUEOUS NITRIC ACID

Density 30° D	4°	Per cent HNO <sub>3</sub> by weight	Grams HNO <sub>3</sub> per 100 c.c.	Density 30° D	4°	Per cent HNO <sub>3</sub> by weight	Grams HNO <sub>3</sub> per 100 c.c.	Density 30° D	4°	Per cent HNO <sub>3</sub> by weight	Grams HNO <sub>3</sub> per 100 c.c.
1.0222		5	5.11	1.2987		50	64.93	1.4761		95	140.22
1.0503		10	10.50	1.3270		55	72.98	1.4952			149.52
1.0794		15	16.19	1.3533		60	81.19				
1.1094		20	22.18	1.3770		65	89.54				
1.1406		25	28.51	1.3983		70	97.88				
1.1727		30	35.18	1.4180		75	106.35				
1.2055		35	42.19	1.4357		80	114.85				
1.2370		40	49.48	1.4518		85	123.40				
1.2680		45	57.06	1.4556		90	131.90				

## AQUEOUS HYDROCHLORIC ACID

Density 30° D	4°	Per cent HCl by weight	Grams HCl per 100 c.c.	Density 30° D	4°	Per cent HCl by weight	Grams HCl per 100 c.c.
1.0006		1	1.00	1.0934		20	21.86
1.0055		2	2.01	1.1034		22	24.27
1.0152		4	4.06	1.1135		24	26.72
1.0248		6	6.15	1.1236		26	29.21
1.0343		8	8.27	1.1336		28	31.74
1.0439		10	10.44	1.1435		30	34.30
1.0537		12	12.64				
1.0636		14	14.89				
1.0735		16	17.17				
1.0834		18	19.50				

## AQUEOUS ACETIC ACID

Density 30° D	4°	Per cent acetic acid by weight	Grams acetic acid per 100 c.c.	Density 30° D	4°	Per cent acetic acid by weight	Grams acetic acid per 100 c.c.
1.0024		5	5.01	1.0416		40	41.66
1.0089		10	10.09	1.0492		50	52.46
1.0151		15	15.22	1.0552		60	63.31
1.0210		20	20.42	1.0590		70	74.13
1.0267		25	25.67	1.0596		80	84.76
1.0320		30	30.96	1.0549		90	94.94
1.0371		35	36.30	1.0380		100	103.80

**AQUEOUS SULPHURIC ACID**

Density 30°	D	Per cent H <sub>2</sub> SO <sub>4</sub> by weight	Grams H <sub>2</sub> SO <sub>4</sub> per 100 c.c.	Density 30°	D	Per cent H <sub>2</sub> SO <sub>4</sub> by weight	Grams H <sub>2</sub> SO <sub>4</sub> per 100 c.c.	Density 30°	D	Per cent H <sub>2</sub> SO <sub>4</sub> by weight	Grams H <sub>2</sub> SO <sub>4</sub> per 100 c.c.
1.0281		5	5.14	1.4372		55	79.04	1.8176		93	169.03
1.0617		10	10.62	1.4898		60	89.38	1.8210		94	171.17
1.0968		15	16.45	1.5446		65	100.40	1.8236		95	173.24
1.1335		20	22.67	1.6014		70	112.10	1.8255		96	175.24
1.1718		25	29.30	1.6597		75	124.50	1.8264		97	177.16
1.2115		30	36.34	1.7170		80	137.36	1.8261		98	178.96
1.2526		35	43.84	1.7678		85	150.26	1.8242		99	180.60
1.2953		40	51.81	1.8038		90	162.34	1.8205		100	182.05
1.3399		45	59.30	1.8090		91	164.62				
1.3872		50	69.36	1.8136		92	166.85				

Aqueous Sodium Hydroxide				Aqueous Ammonia				Aqueous Sodium Carbonate			
Density 30° D	4°	Per cent NaOH by weight	Grams NaOH per 100 c.c.	Density 30° D	4°	Per cent NH <sub>3</sub> by weight	Grams NH <sub>3</sub> per 100 c.c.	Density 30° D	4°	Per cent Na <sub>2</sub> CO <sub>3</sub> by weight	Grams Na <sub>2</sub> CO <sub>3</sub> per 100 c.c.
1.0177	2	2.03	0.9939	1		1.0	1.0058	1		1	
1.0393	4	4.16	0.9895	2		2.0	1.0159	2		2.03	
1.0609	6	6.36	0.9811	4		3.9	1.0363	4		4.14	
1.0826	8	8.66	0.9730	6		5.8	1.0568	6		6.34	
1.1043	10	11.04	0.9651	8		7.7	1.0775	8		8.62	
1.1261	12	13.51	0.9575	10		9.6	1.0986	10		10.10	
1.1480	14	16.07	0.9501	12		11.4	1.1200	12		13.44	
1.1699	16	18.72	0.9430	14		13.2	1.1417	14		15.98	
1.1918	18	21.45	0.9362	16		15.0	1.1636	16		18.62	
1.2136	20	24.27	0.9295	18		16.8	1.1859	18		21.34	
1.2680	25	31.70	0.9229	20		18.5	1.2086	20		24.17	
1.3217	30	39.65	0.9164	22		20.2	1.2317	22		27.09	
1.3733	35	48.06	0.9101	24		21.8	1.2552	24		30.12	
1.4232	40	56.92	0.9040	26		23.5	1.2790	26		33.25	
1.4710	45	66.20	0.8980	28		25.1	1.3031	28		36.48	
1.5181	50	75.90	0.8920	30		26.8	1.3274	30		39.82	

## Specific Gravities and percentages of weight of aqueous Ethyl Alcohol

Percentage by weight	D 25° 4°	Grams of alcohol per 100 c.c.	D 30° 4°	Grams of alcohol per 100 c.c.
5	0.98817	4.94	0.98670	4.93
10	0.98043	9.80	0.97875	9.79
15	0.97334	14.60	0.97133	4.56
20	0.96639	19.32	0.96395	19.30
25	0.95895	23.97	0.95607	23.90
30	0.95067	28.52	0.94741	28.42
35	0.94146	32.95	0.93790	32.82
40	0.93148	37.25	0.92770	37.10
45	0.92085	41.43	0.91692	41.26
50	0.90985	45.49	0.90580	45.29
55	0.89850	49.41	0.89437	49.19
60	0.88699	53.21	0.88278	42.96
65	0.87527	56.89	0.87100	56.61
70	0.86340	60.43	0.85908	61.13
75	0.85134	63.85	0.84698	63.52
80	0.83911	67.12	0.83473	66.77
85	0.82660	70.26	0.82220	69.88
90	0.81362	73.22	0.80922	72.83
95	0.79991	76.00	0.79555	75.57
96	0.79706	76.51	0.79271	76.10
97	0.79415	77.03	0.78981	76.61
98	0.79117	77.53	0.78684	77.11
99	0.78814	78.02	0.78382	77.60
100	0.78506	78.50	0.78075	78.07

## Vapour Pressure of Caustic Potash solutions in mm.

Temperature	Parts KOH in 100 parts water		
	30	40	49
20	13.93	12.40	10.75
21	14.82	13.20	11.44
22.5	16.25	14.47	12.55
23	16.75	14.92	12.94
24	17.80	15.86	13.76
25	18.90	16.85	14.62
26	20.07	17.89	15.53
27.5	21.94	19.57	17.00
28.6	23.44	20.89	18.16
29	23.96	21.38	18.59
30	25.40	22.67	19.72

Weight (in Milligrams) of Nitrogen in one Cubic Centimetre of the Moist Gas Measured at Temperature  $t^{\circ}\text{C}$ , and  $p$  mm.  
Pressure

$t$	$p$ 722	724	726	728	730	732	734	736	738	740	742	744	746	748	750	752	754	756
20°	1.080	1.083	1.086	1.089	1.092	1.095	1.099	1.102	1.105	1.108	1.111	1.114	1.117	1.120	1.123	1.126	1.129	1.132
21°	1.075	1.078	1.081	1.084	1.087	1.090	1.093	1.096	1.099	1.102	1.105	1.108	1.111	1.115	1.118	1.121	1.124	1.127
22°	1.069	1.073	1.076	1.079	1.082	1.085	1.088	1.091	1.094	1.097	1.100	1.103	1.106	1.109	1.112	1.115	1.118	1.121
23°	1.064	1.067	1.070	1.073	1.076	1.079	1.082	1.085	1.088	1.091	1.094	1.097	1.100	1.103	1.106	1.109	1.112	1.115
24°	1.058	1.061	1.064	1.067	1.070	1.073	1.076	1.080	1.083	1.086	1.089	1.092	1.095	1.098	1.101	1.104	1.107	1.110
25°	1.053	1.056	1.059	1.062	1.065	1.068	1.071	1.074	1.077	1.080	1.083	1.086	1.089	1.092	1.095	1.098	1.101	1.104
26°	1.047	1.050	1.053	1.056	1.059	1.062	1.065	1.068	1.071	1.074	1.077	1.080	1.083	1.086	1.089	1.092	1.095	1.098
27°	1.041	1.044	1.047	1.050	1.053	1.056	1.059	1.062	1.065	1.068	1.071	1.074	1.077	1.080	1.083	1.086	1.089	1.092
28°	1.035	1.038	1.041	1.044	1.047	1.050	1.053	1.056	1.059	1.062	1.065	1.068	1.071	1.074	1.077	1.080	1.083	1.086
29°	1.030	1.033	1.036	1.039	1.042	1.044	1.047	1.050	1.053	1.056	1.059	1.062	1.065	1.068	1.071	1.074	1.077	1.080
30°	1.024	1.027	1.029	1.032	1.035	1.038	1.041	1.044	1.047	1.050	1.053	1.056	1.059	1.062	1.065	1.068	1.071	1.074

$t$	$p$ 758	760	762	764	766	768	770
20°	1.135	1.138	1.141	1.145	1.148	1.151	1.154
21°	1.130	1.133	1.136	1.139	1.142	1.145	1.148
22°	1.124	1.127	1.130	1.133	1.136	1.139	1.143
23°	1.119	1.122	1.125	1.128	1.131	1.134	1.137
24°	1.113	1.116	1.119	1.122	1.125	1.128	1.131
25°	1.107	1.110	1.113	1.116	1.119	1.122	1.125
26°	1.101	1.104	1.107	1.110	1.113	1.116	1.119
27°	1.095	1.098	1.101	1.104	1.107	1.110	1.113
28°	1.089	1.092	1.095	1.098	1.101	1.104	1.107
29°	1.083	1.086	1.089	1.092	1.095	1.098	1.101
30°	1.077	1.080	1.083	1.086	1.089	1.092	1.095



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